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(54) Title: COMPLEX HYDROPHOBE COMPOUNDS, MACROMONOMERS AND MACROMONOMER-CONTAINING POLYMERS

(57) Abstract

This invention relates to polymers which comprise the reaction product of: (A) about 0-99.9 weight percent of one or more nonionic, cationic, anionic or amphoteric monomers; (B) about 0-99.9 weight percent of one or more monoethylenically unsaturated monomers different from (A); (C) about 0.1-100 weight percent of one or more monoethylenically unsaturated macromonomers different from (A) and (B); and (D) about 0-20 weight percent or greater of one or more polyethylenically unsaturated monomers different from (A), (B) and (C). When the polymers are added to latex paints and the pH adjusted, the viscosity of the paint is increased, brush drag is increased, and the paint rheology is otherwise improved. This invention also relates to macromonomer compounds useful as copolymerizable monomers in various polymerization methods and as emulsifiers in the emulsion or suspension polymerization of various monomers to produce an aqueous suspension of polymer particles. This invention further relates to complex hydrophobe compounds and to alkoxylation products, i.e., condensation reaction products of alkylene oxides and complex hydrophobe compounds having at least one active hydrogen and to alkoxylation products.

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COMPLEX HYDROPHOBE COMPOUNDS, MACROMONOMERS AND MACROMONOMER-CONTAINING POLYMERS

Brief Summary of the Invention

Technical Field

This invention relates to polymers which contain macromonomers and which can contain nonionic, cationic, anionic and/or amphoteric monomers. The polymers are especially useful as thickeners for aqueous systems, e.g., certain of the polymers are soluble in, or swelled by, an aqueous alkaline medium to provide thickeners for use in aqueous coating compositions, especially latex paints. This invention also relates to macromonomers containing complex hydrophobic groups and to complex hydrophobe compounds.

Background of the Invention

Thickeners for aqueous systems are needed for various purposes, such as for architectual coatings, industrial coatings, automotive coatings and the like to improve rheology of the coatings. Hydroxyethyl cellulose is a well known thickener for aqueous systems, but it has various deficiencies in that excessive amounts must be used and the rheology of the thickened system is inadequate. Various ethoxylated carboxyl-functional polymers which form alkali soluble thickeners are also known, but these have various deficiencies, including inadequate hydrolytic stability.

It has long been desired to provide superior thickeners for aqueous systems which are highly efficient, which better resist hydrolysis, and which provide better rheology. This is achieved herein by providing new polymers which possess these desired characteristics.

Disclosure of the Invention

This invention relates in part to polymers (I) comprising the reaction product of:

(A)) about 0-99.9, preferably about 10-70, weight percent of one or more nonnionic, cationic, anionic and/or amphoteric monomers;

(B)) about 0-99.9, preferably about 30-85, weight percent of one or more monnoethylenically unsaturated monomers, typically ethyl acrylate, ddifferent from component (A);

(C)) about 0.1-100, preferably about 5-60, weight percent of one or more moonoethylenically unsaturated macromonomers different from ccomponents (A) and (B); and

(D)) about 0-20, preferably about 0-10, weight percent or greater of one oor more polyethylenically unsaturated monomers, typically trimetlthylol propane triacrylate, different from components (A), (B) and (C).).

Thiis invention also relates in part to an emulsion of the above-identifiedd polymer (I) in water, which emulsion is useful as a thickening agennt in aqueous compositions. In order to obtain the thickening effectt, the polymer (I) is dissolved in the aqueous composition to bbe thickened.

Thiis invention further relates in part to an aqueous composition, annd more particularly an improved latex paint composition conntaining the above-defined polymer (I).

Thiis invention yet further relates in part to a process for thickening an aaqueous composition which comprises adding the above-defined ppolymer (I) to an aqueous composition and dissolving the polymer (I)) in the aqueous composition.

TThis invention relates in part to polymers (II) comprising the reaction proodduct of:

((A) about 1-99.9, preferably about 10-70, weight percent of one or more alppha, beta-monoethylenically unsaturated carboxylic acids, typically methaacrylic acid;

(B) about 0-98.9, preferably about 30-85, weight percent of one or more monoethylenically unsaturated monomers, typically ethyl acrylate, different from component (A);

(C) about 0.1-99, preferably about 5-60, weight percent of one or more monoethylenically unsaturated macromonomers different from components (A) and (B); and

(D) about 0-20, preferably about 0-10, weight percent or greater of one or more polyethylenically unsaturated monomers, typically trimethylol propane triacrylate, different from components (A), (B) and (C).

This invention also relates in part to an emulsion of the above-identified polymer (II) in water, which emulsion is useful as a thickening agent in aqueous compositions. In order to obtain the thickening effect, the polymer (II) is dissolved in the aqueous composition to be thickened.

This invention further relates in part to an aqueous composition, and more particularly an improved latex paint composition containing the above-defined polymer (II).

This invention yet further relates in part to a process for thickening an aqueous composition which comprises adding the above-defined polymer (II) to an aqueous composition and dissolving the polymer (II) in the aqueous composition.

This invention relates in part to polymers (III) comprising the reaction product of:

(A) from 1 to about 99.9 weight percent, preferably from about 60 to 95 weight percent and more preferably from about 70 to 95 weight percent, of one or more nonionic monoethylenically unsaturated monomers, for example, acrylamide, N,N-dimethyl acrylamide, vinyl pyrrolidone and hydroxyethyl acrylate; and

(B) from about 0.1 weight percent to 99 weight percent, preferably from about 5 to 40 weight percent and more preferably from about 5 to 30 weight percent, of one or more

monoethylenically unsaturated macromonomers different from component (A).

This invention also relates in part to an emulsion of the above-identified polymer (III) in water, which emulsion is useful as a thickening agent in aqueous compositions. In order to obtain the thickening effect, the polymer (III) is dissolved in the aqueous composition to be thickened.

This invention further relates in part to an aqueous composition, and more particularly an improved latex paint composition containing the above-defined polymer (III).

This invention yet further relates in part to a process for thickening an aqueous composition which comprises adding the above-defined polymer (III) to an aqueous composition and dissolving the polymer (III) in the aqueous composition.

This invention relates to compounds represented by the formula:

$$R^1\text{-}(OR^2)_z\text{-}R^3\text{-}(\text{-}\overset{\displaystyle R^4}{\overset{|}{C}}=CR^5R^6 \qquad \text{(I)}$$

wherein:

R^1 is a monovalent residue of a substituted or unsubstituted complex hydrophobe compound;

each R^2 is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue;

R^3 is a substituted or unsubstituted divalent hydrocarbon residue;

R^4, R^5 and R^6 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue; and

z is a value of 0 or greater.

This invention relates to compounds represented by the formula:

$$\begin{array}{l} R_1\text{-}(O\text{-}CH_2)_a \\ \qquad\quad \diagdown \\ \qquad\qquad R_3\text{-}(OR_4)_x\text{-}(OR_5)_y\text{-}OR_6 \\ \qquad\quad \diagup \\ R_2\text{-}(O\text{-}CH_2)_b \end{array} \qquad \text{(i)}$$

wherein R_1 and R_2 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue, R_3 is a substituted or unsubstituted divalent or trivalent hydrocarbon residue, each R_4 is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, each R_5 is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, R_6 is hydrogen, a substituted or unsubstituted monovalent hydrocarbon residue or an ionic substituent, a and b are the same or different and are a value of 0 or 1, and x and y are the same or different and are a value of 0 or greater; provided (i) at least two of R_1, R_2, R_3, R_4, R_5 and R_6 are a hydrocarbon residue having greater than 2 carbon atoms in the case of R_1, R_2 and R_6 or having greater than 2 pendant carbon atoms in the case of R_3, R_4 and R_5, (ii) at least one of R_4 and R_5 is other than $-CH_2CH_2-$ when R_1 and R_2 are nonylphenyl, R_3 is $>CH-$, R_6 is hydrogen or SO_3, a is a value of 1, b is a value of 1, and at least one of x and y is a value of 1 or greater, and (iii) R_4 is $-CH_2CH_2-$ and x is a value of at least 2 when R_1 is hexadecyl, R_2 is tetradecyl, R_3 is $>CH-$, at least one R_5 is $-CH_2CH(\text{tetradecyl})-$, R_6 is hydrogen, y is a value of 1 or greater, a is a value of 1, and b is a value of 0.

This invention also relates to compounds represented by the formula:

$$\begin{array}{l} R_7\text{-}(OCH_2)_d\text{-}R_9\text{-}(OR_{10})_f\text{-}OR_{11} \\ \qquad\qquad\quad | \\ \qquad\qquad\quad R_{15} \\ \qquad\qquad\quad | \\ R_8\text{-}(OCH_2)_e\text{-}R_{12}\text{-}(OR_{13})_g\text{-}OR_{14} \end{array} \qquad \text{(ii)}$$

wherein R_7 and R_8 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue, R_{11} and R_{14} are the same or different and are hydrogen, a substituted or unsubstituted monovalent hydrocarbon residue or an ionic substituent, R_9 and R_{12} are the same or different and are a substituted or unsubstituted divalent or trivalent hydrocarbon residue, each R_{10} is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, each R_{13} is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, R_{15} is a substituted or unsubstituted divalent hydrocarbon residue, d and e are the same or different and are a value of 0 or 1, and f and g are the same or different and are a value of 0 or greater; provided at least two of R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14} and R_{15} are a hydrocarbon residue having greater than 2 carbon atoms in the case of R_7, R_8, R_{11} and R_{14} or having greater than 2 pendant carbon atoms in the case of R_9, R_{10}, R_{12}, R_{13} and R_{15}.

This invention further relates to alkoxylation product mixtures which can have relatively narrow alkoxylation product distributions. These product mixtures are relatively free from large amounts of substantially higher alkoxylation moieties, i.e, those having at least three more alkoxyl groups than the average peak

alkoxylate specie. Advantageously, these narrow distributions can be obtained where the most prevalent alkoxylation moiety has four or greater alkoxy units, that is, in the regions which generally have a relatively wide range of alkoxylation species.

<u>Detailed Description</u>

Illustrative nonionic, cationic, anionic and amphoteric monomers useful in this invention include those monomers which impart water solubility to the polymer. Preferably, a large proportion of component (A) is employed to impart water solubility to the polymers of this invention. The key to water solubility lies in positioning sufficient numbers of hydrophilic functional groups along the backbone or side chains. Suitable functional groups which impart water solubility and suitable nonionic, cationic, anionic and amphoteric monomers useful in this invention are described in Water-Soluble Polymers, Synthesis, Solution Properties and Applications, ACCS Symposium Series 467, American Chemical Society (1991), which is incorporated herein by reference. Mixtures of nonionic, cationic, anionic and amphoteric monomers may be employed in this invention, e.g., mixtures of nonionic monomers, mixtures of nonionic and cationic monomers, etc.

Illustrative nonionic monomers useful in this invention include, for example, acrylamide, N, N-dimethyl acrylamide, vinyl pyrrolidone, ethylene oxide, vinyl alcohol, vinyl acetate, N-vinylpyrrolidinone, hydroxyethyl acrylate and the like including mixtures thereof. Illustrative cationic monomers useful in this invention include, for example, ammonium, sulfonium and phosphonium salts, preferably quarternary ammonium salts such as diallyldimethylammonium chloride, diallyldiethylammonium chloride, diethylaminoethyl methacrylate, dimethylaminoethyl methacrylate, methacryloyloxyethyltrimethylammonium sulfate, methacryloyloxyethyltrimethylammonium chloride, 3-

(methacrylamido)propyltrimethylammonium chloride and the like including mixtures thereof.

Illustrative anionic monomers useful in this invention include, for example, acrylic acid, methacrylic acid, maleic anhydride, p-styrene carboxylic acids, p-styrene sulfonic acids, vinyl sulfonic acid, 2-sulfoethyl methacrylate, 3-sulfopropyl methacrylate, 3-sulfopropyl acrylate, 2-acrylamido-2-methylpropane sulfonic acid, 3-acrylamido-3-methylbutanoic acid and the like including mixtures thereof and salts thereof. Illustrative amphoteric monomers useful in this invention contain zwitterions on the same monomers, i.e., betaines, or along the same polymer backbone, i.e., ampholytes, and include, for example, N,N-dimethyl-N-methacryloxyethyl-N-(3-sulfopropyl)ammonium-betain, N,N-dimethyl-N-methacrylamidopropyl-N-(3-sulfopropyl)ammonium-betain, 1-(3-sulfopropyl)-2-vinylpyridinium-betain, 3-(2-acrylamido-2-methyl-propyldimethylammonio)-1-propanesulfonate, N-vinylpyrrolidone-co-N,N-dimethyl-N-methacroyloxyethylammoniopropanesulfonate, N-vinylpyrrolidone- co-N,N-dimethyl-N-methacroylamidopropylammonio- propanesulfonate, N-vinylpyrrolidone-co-2-vinylpyridinio-propanesulfonate and the like including mixtures thereof.

Preferably, a large proportion of one or more alpha, beta-monoethylenically unsaturated carboxylic acid monomers can be present in the polymers of this invention. Various carboxylic acid monomers can be used, such as acrylic acid, methacrylic acid, ethacrylic acid, alpha-chloroacrylic acid, crotonic acid, fumaric acid, citraconic acid, mesaconic acid, itaconic acid, maleic acid and the like including mixtures thereof. Methacrylic acid is preferred. A large proportion of carboxylic acid monomer is essential to provide a polymeric structure which will solubilize and provide a thickener when reacted with an alkali like sodium hydroxide.

The polymers of this invention can also contain a significant proportion of one or more monoethylenically unsaturated monomers. The preferred monomers provide water insoluble polymers when homopolymerized and are illustrated by acrylate and methacrylate esters, such as ethyl acrylate, butyl acrylate or the corresponding methacrylate. Other monomers which can be used are styrene, alkyl styrenes, vinyl toluene, vinyl acetate, vinyl alcohol, acrylonitrile, vinylidene chloride, vinyl ketones and the like. Nonreactive monomers are preferred, those being monomers in which the single ethylenic group is the only group reactive under the conditions of polymerization. However, monomers which include groups reactive under baking conditions or with divalent metal ions such as zinc oxide may be used in some situations, like hydroxyethyl acrylate.

Other illustrative monoethylenically unsaturated monomers useful in this invention include, for example, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, n-amyl methacrylate, sec-amyl methacrylate, hexyl methacrylate, lauryl methacrylate, stearyl methacrylate, ethyl hexyl methacrylate, crotyl methacrylate, cinnamyl methacrylate, oleyl methacrylate, ricinoleyl methacrylate, hydroxy ethyl methacrylate, hydroxy propyl methacrylate, vinyl propionate, vinyl butyrate, vinyl tert-butyrate, vinyl caprate, vinyl stearate, vinyl laurate, vinyl oleate, vinyl methyl ether, vinyl ethyl ether, vinyl n-propyl ether, vinyl iso-propyl ether, vinyl n-butyl ether, vinyl iso-butyl ether, vinyl iso-octyl ether, vinyl phenyl ether, α-chlorovinyl phenyl ether, vinyl β-naphthyl ether, methacryonitrile, acrylamide, methacrylamide, N-alkyl acrylamides, N-aryl acrylamides, N-vinyl pyrrolidone, N-vinyl-3-morpholinones, N-vinyl-oxazolidone, N-vinyl-imidazole and the like including mixtures thereof.

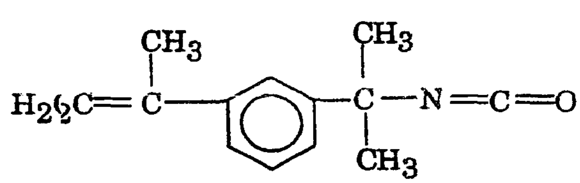
The macromonomers useful in this invention can be represented by the formula (I) above. The macromonomer

compounds useful in this invention can be prepared by a number of conventional processes, except for inclusion of the complex hydrophobe compounds described herein. Illustrative processes are described, for example, in U.S. Patent Nos. 4,514,552, 4,600,761, 4,569,965, 4,384,096, 4,268,641, 4,138,381, 3,894,980, 3,896,161, 3,652,497, 4,509,949, 4,226,754, 3,915,921, 3,940,351, 3,035,004, 4,429,097, 4,421,902, 4,167,502, 4,764,554, 4,616,074, 4,464,524, 3,657,175, 4,008,202, 3,190,925, 3,794,608, 4,338,239, 4,939,283 and 3,499,876. Other macromonomer compounds which may be useful in this invention include complex hydrophobe-containing oligomers dislcosed in copending U.S. Patent Application Serial No. 07/887,646, filed May 29, 1992, which is incorporated herein by reference.

In a preferred embodiment, the macromonomer compounds of this invention can be prepared by coupling a compound represented by the formula:

$$R^1\text{-}(OR^2)_z\text{-}OH \qquad \text{(II)}$$

with an ethylenically unsaturated compound such as alpha, alpha-dimethyl meta isopropenyl benzyl isocyanate having the formula:

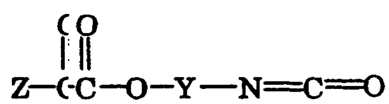


(III)

wherein R^1, R^2 and z are as defined above. This coupling reaction can be carried out in the presence of a catalyst such as bismuth octoate, dibutyl tin dilaurate and the like. The coupling reaction can

be conducted at a a temperature of about 50°C to about 150°C and a pressure of abouut 1 atmosphere or so. Stoichiometric amounts of starting materiaals can generally be employed.

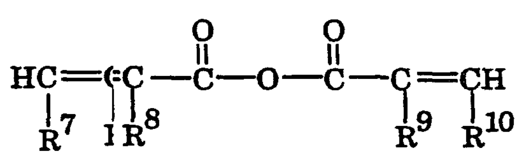
It t is understood that surfactants or alcohols with more than one hydroxxyl, or compounds that have amine functionality, and the like can be uused. Other unsaturated mono-, di-, and triisocyanates, ssuch as isocyanato ethyl methacrylate, allyl isocyanate, and the like can also be used. Other monoisocyanates useful in preparring macromonomer compounds of this invention have the formulda:



(IV)

where Y is a suhbstituted or unsubstituted divalent hydrocarbon residue such as defined for R^3 herein, and Z is the residue of an ethylenically unnsaturated compound such as CH_2=CH-, CH_2=C(CH_3)- onr CH_2=CH-CH_2-.

Irin another embodiment, the compound represented by formula (II) cann react with an alpha, beta-unsaturated dicarboxylic acid or acid anhhydride having the formula:

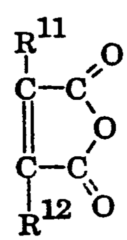


(V)

to produce an eester, wherein R^7, R^8, R^9 and R^{10} are the same or different and arre hydrogen or a substituted or unsubstituted hydrocarbon reesidue, preferably an alkyl residue. If R^7, R^8, R^9 and R^{10} are hydroggen, then the acrylic ester is formed; if R^7 and R^{10} are hydrogen and RR^8 and R^9 are methyl, then the methacrylic ester is formed; if R^7 annd R^{10} are methyl and R^8 and R^9 are hydrogen, then the crotonic estter is formed. Other anhydrides, such as itaconic anhydride, crottonic anhydride, allyl succinic, methylene malonic, and the like cann also be used.

TThis reaction can be carried out in the presence of a catalyst such ass pyridine, triethylamine and the like. The reaction can be conducteed at a temperature of about ambient to about 120°C and a pressure of about 1 atmosphere or so. Stoichiometric amounts of starting matderials can generally be employed.

IIn addition, cyclic alpha, beta-unsaturated dicarboxylic aciid anhydrides, such as maleic anhydride can also be used:



(VI)

wherein R^{11} annd R^{12} are the same or different and are hydrogen or a substituted or uunsubstituted hydrocarbon residue, preferably halogen, cyanoggen, hydroxyl, lactam and lactone groups, aryl,

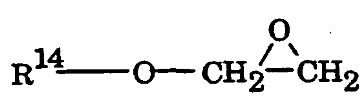
aralkyl, substituted alkyl, aryl or aralkyl groups, such as methyl, ethyl, propyl, octyl, decyl, phenyl, tolyl, xylyl, benzyl, cyclohexyl, and the like, or $-SO_3H$. Examples of such compounds are chloromaleic anhydride, citraconic anhydride, fumaric anhydride, mesaconic anhydride, phenyl maleic anhydride, benzyl maleic anhydride, sulfomaleic anhydride, aconitic anhydride, and the like.

Other synthetic routes such as transesterification or nucleophilic substitution reactions can be used. For example, the compound represented by formula (II) can react with an acid halide having the formula:

$$R^{13}-\overset{\overset{\displaystyle O}{\|}}{C}-X \qquad \text{(VII)}$$

wherein R^{13} is the residue of an ethylenically unsaturated compound such as $CH_2{=}CH-$, $CH_2{=}C(CH_3)-$ or $CH_2{=}CH-CH_2-$, and X is NH_2 or halogen such as chloro, bromo, fluoro or iodo. This reaction can be carried out in the presence of a catalyst such as pyridine, triethylamine and the like. The reaction can be conducted at a temperature of about ambient to about 120°C and a pressure of about 1 atmosphere or so. Stoichiometric amounts of starting materials can generally be employed.

In yet another embodiment, the compound represented by formula (II) can react with an epoxide having the formula:



(VIII)

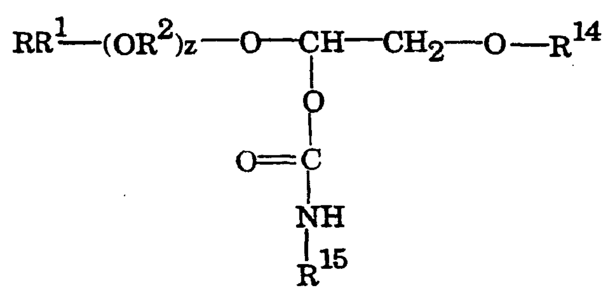
wherein R^{14} is a substituted or unsubstituted hydrocarbon residue, preferably the rresidue of an ethylenically unsaturated compound such as CH_2=CH-, CH_2=C(CH_3)- or CH_2=CH-CH_2-. If R^{14} is not a reactive substitutuent, then the resulting product having the formula:

$$R^1\text{-}(OR^2)_z\text{-}O\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_2\text{-}O\text{-}R^{14} \qquad \text{(IX)}$$

can be reacted with an unsaturated hydrocarbon compound such as an isocyanate hhaving the formula:

$$R^{15}\text{-}N{=}C{=}O \qquad \text{(X)}$$

to provide a maacromonomer compound having the formula:



(XI)

wherein R^1, R^2, R^{14} and z are as defined above and R^{15} is the residue of an ethylenicaally unsaturated compound such as CH_2=CH-,

CH_2=C(CH_3)- or CH_2=CH-CH_2-. This reaction can be carried out in the presence of a catalyst such as bismuth octoate, dibutyl tin dilaurate and the like. The reaction can conducted at a temperature of about ambient to about 120°C and a pressure of about 1 atmosphere or so. Stoichiometric amounts of starting materials can generally be employed.

The macromonomer can be prepared by a neat process (without solvent), or in solution. When neat, the complex hydrophobe compound having at least one active hydrogen such as a surfactant or poly(oxyethylene) derivative can be melted and sparged with nitrogen before charging the reactants to remove moisture; when in solution, water is removed by way of an azeotrope. Then the catalyst and capping materials are charged, and the reaction mixture heated until the reaction goes to completion. The reaction stoichiometry of the surfactant and the capping material may be optimized to promote thickener efficiency and minimize coagulum formation during the subsequent polymerization. Afterwards, water can be added to the neat macromonomer to lower its viscosity. The material made in solution is recovered as a solid after solvent removal, or can be put into aqueous solution by the addition of water during azeotropic distillation.

The unsaturation portion of the macromonomer compounds of this invention can be derived from olefinically unsaturated compounds containing at least one activated carbon-to-carbon olefinic double bond which readily functions in polymerization of the macromonomer compound. Suitable olefinically unsaturated compounds include, for example, acrylic acids typified by acrylic acid itself, methacrylic acid, ethacrylic acid, alpha-chloro-acrylic acid, alpha-cyano acrylic acid, beta-methyl acrylic acid (crotonic acid), alpha-phenyl acrylic acid, beta-acryloxy propionic acid, sorbic acid, alpha-chloro sorbic acid, angelic acid, cinnamic acid, p-chloro cinnamic acid, beta-styryl acrylic acid (1-

carboxy-4-phenyl butadiene-1,3), itaconic acid, citraconic acid, mesaconic acid, glutaconic acid, aconitic acid, maleic acid, fumaric acid, and tri-carboxy ethylene. Also included are polycarboxylic acids and those acid anhydrides, such as maleic anhydride, wherein the anhydride group is formed by the elimination of one molecule of water from two carboxyl groups located on the same polycarboxylic acid molecule.

Suitable acid anhydrides include alpha, beta-unsaturated dicarboxylic acid anhydrides such as maleic anhydride, chloromaleic anhydride, citraconic anhydride (methyl maleic), fumaric anhydride, phenyl maleic anhydride, benzyl maleic anhydride, sulfomaleic anhydride, aconitic anhydride and the like. Other unsaturated anhydrides useful in this invention include itaconic anhydride, methylene malonic anhydride, allyl succinic anhydride and the like.

Illustrative substituted and unsubstituted divalent hydrocarbon residues represented by R^2 in formula (I) above include those described for the same type of substituents in formulae (i) and (ii) below. Illustrative substituted and unsubstituted monovalent hydrocarbon residues represented by R^4, R^5 and R^6 in formula (I) above include those described for the same type of substituents in formulae (i) and (ii) below.

Illustrative R^3 substituents include, for example, the organic residue of ethers, esters, urethanes, amides, ureas, urethanes, anhydrides and the like including mixtures thereof. The R^3 substituent can be generally described as a "linkage" between the complex hydrophobe bearing surfactant or alcohol, and the unsaturation portion of the macromonomer compound. Preferred linkages include the following: urethane linkages from the reaction of an isocyanate with a nonionic surfactant; urea linkages from the reaction of an isocyanate with an amine bearing surfactant; unsaturated esters of surfactants such as the esterification product of

a surfactant witlth of an unsaturated carboxylic acid or an unsaturated anhhydride; unsaturated esters of alcohols; esters of ethyl acrylate oligomeiers, acrylic acid oligomers, and allyl containing oligomers; half eesters of surfactants such as those made by the reaction of a surrfactant with maleic anhydride; unsaturated ethers prepared by reaacting vinyl benzyl chloride and a surfactant or by reacting an allyl glycidyl ether with a surfactant, alcohol, or carboxylic acid.

Thee oxyalkylene moieties included in the macromonomer compounds of formula (I) may be homopolymers or block or random copolymers of straight or branched alkylene oxides. Mixtures of alkyylene oxides such as ethylene oxide and propylene oxide may be emnployed. It is understood that each R^2 group in a particular substititutent for all positive values of z can be the same or different.

Thee complex hydrophobe compounds having at least one active hydrogen useful in preparing the macromonomer compounds useful in this inwvention can be represented by the formula:

$$\begin{array}{l} R_1\text{-}(O\text{-}CH_2)_a \\ \qquad\qquad \diagdown \\ \qquad\qquad\quad R_3\text{-}(OR_4)_x\text{-}(OR_5)_y\text{-}OR_6 \\ \qquad\qquad \diagup \\ R_2\text{-}(O\text{-}CH_2)_b \end{array} \qquad \text{(i)}$$

wherein R_1 and R_2 are the same or different and are hydrogen or a substituted or unnsubstituted monovalent hydrocarbon residue, R_3 is a substituted or unnsubstituted divalent or trivalent hydrocarbon residue, each R_4 is the saame or different and is a substituted or unsubstituted divalent hydrocaarbon residue, each R_5 is the same or different and is a

substituted or unsubstituted divalent hydrocarbon residue, R_6 is hydrogen, a substituted or unsubstituted monovalent hydrocarbon residue or an ionic substituent, a and b are the same or different and are a value of 0 or 1, and x and y are the same or different and are a value of 0 or greater; provided at least two of R_1, R_2, R_3, R_4, R_5 and R_6 are a hydrocarbon residue having greater than 2 carbon atoms in the case of R_1, R_2 and R_6 or having greater than 2 pendant carbon atoms in the case of R_3, R_4 and R_5. For purposes of the complex hydrophobes of formula (i) above, at least one of R_4 and R_5 is other than $-CH_2CH_2-$ when R_1 and R_2 are nonylphenyl, R_3 is $>CH-$, R_6 is hydrogen or SO_3, a is a value of 1, b is a value of 1, and at least one of x and y is a value of 1 or greater. Also for purposes of the complex hydrophobes of formula (i) above, R_4 is $-CH_2CH_2-$ and x is a value of at least 2 when R_1 is hexadecyl, R_2 is tetradecyl, R_3 is $>CH-$, at least one R_5 is $-CH_2CH$(tetradecyl)-, R_6 is hydrogen, y is a value of 1 or greater, a is a value of 1, and b is a value of 0. For purposes of the homopolymers and macromonomers of formula (I) above, when z is a value of 0 and R^1 is the residue of a complex hydrophobe of formula (i) in which R_1 is hexadecyl, a is a value of 1, R_2 is tetradecyl, b is a value of 0, R_3 is $>CH-$, R_4 is $-CH_2CH$(tetradecyl)-, x is a value of 1, R_5 is $-CH_2CH_2-$, y is a value of 34 and R_6 is hydrogen, then the $-R^3(R^4)C=CR^5R^6$ portion of the macromonomer is other than the residue of maleic anhydride. Also for purposes of the homopolymers and macromonomers of formula (I) above, when R^2 and R^3 are hydrogen, z is a value of 34 and R^1 is the residue of a complex hydrophobe of formula (i) in which R_1 is hexadecyl, a is a value of 1, R_2 is tetradecyl, b is a value of 0, R_3 is $>CH-$, R_4 is $-CH_2CH$(tetradecyl)-, x is a value of 1, y is a value of 0 and R_6 is hydrogen, then the $-R^3-(R^4)C=CR^5R^6$ portion of the macromonomer is other than the residue of maleic anhydride. For purposes of polymers (I) and (II) above, when z is a value of 0 and R^1 is the residue of a complex hydrophobe of formula (i) in which R_1 is hexadecyl, a is a value of 1, R_2 is tetradecyl, b is a value of 0, R_3 is $>CH-$, R_4 is $-CH_2CH$(tetradecyl)-, x is a value of 1, R_5 is $-CH_2CH_2-$, y is a value of 34, R_6 is hydrogen, and the $-R^3-(R^4)C=CR^5R^6$

portion of the macromonomer is the residue of maleic anhydride, then the polymers of this invention are other than a terpolymer of said macromonomer, styrene and maleic anhydride. Also for purposes of polymers (I) and (II) above, when R^2 is $-CH_2CH_2-$, z is a value of 34 and R^1 is the residue of a complex hydrophobe of formula (i) in which R_1 is hexadecyl, a is a value of 1, R_2 is tetradecyl, b is a value of 0, R_3 is $>CH-$, R_4 is $-CH_2CH(\text{tetradecyl})-$, x is a value of 1, y is a value of 0, R_6 is hydrogen and the $-R^3-(R^4)OC=CR^5R^6$ portion of the macromonomer is the residue of maleic anhydride, then the polymers of this invention are other than a terpolymer of said macromonomer, styrene and maleic anhydride.

Other complex hydrophobe compounds having at least one active hydrogen useful in preparing the macromonomer compounds useful in this invention can be represented by the formula:

$$\begin{array}{l} R_7\text{-}(OCH_2)_d\text{-}R_9\text{-}((OR_{10})_f\text{-}OR_{11} \\ \qquad\qquad\quad | \\ \qquad\qquad\quad R_{15}\,; \\ \qquad\qquad\quad | \\ R_8\text{-}(OCH_2)_e\text{-}R_{12}\text{-}(OR_{13})_g\text{-}OR_{14} \end{array} \qquad \text{(ii)}$$

wherein R_7 and R_8 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue, R_{11} and R_{14} are the same or different and are hydrogen, a substituted or unsubstituted monovalent hydrocarbon residue or an ionic substituent, R_9 and R_{12} are the same or different and are a substituted or unsubstituted divalent or trivalent hydrocarbon residue, each R_{10} is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, each R_{13} is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, R_{15} is a substituted or unsubstituted divalent hydrocarbon residue, d and e are the same or different and are a value of 0 or 1,

and f and g are the same or different and are a value of 0 or greater; provided at least two of R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14} and R_{15} are a hydrocarbon residue having greater than 2 carbon atoms in the case of R_7, R_8, R_{11} and R_{14} or having greater than 2 pendant carbon atoms in the case of R_9, R_{10}, R_{12}, R_{13} and R_{15}.

Illustrative substituted and unsubstituted monovalent hydrocarbon residues contain from 1 to about 50 carbon atoms or greater and are selected from alkyl radicals including linear or branched primary, secondary or tertiary alkyl radicals, such as methyl, ethyl, n-propyl, isopropyl, amyl, sec-amyl, t-amyl, 2-ethylhexyl and the like; aryl radicals such as phenyl, naphthyl and the like; arylalkyl radicals such as benzyl, phenylethyl, tri-phenylmethylethane and the like; alkylaryl radicals such as octylphenyl, nonylphenyl, dodecylphenyl, tolyl, xylyl and the like; and cycloalkyl radicals such as cyclopentyl, cyclohexyl, cyclohexylethyl and the like. The permissible hydrocarbon residues may contain fluorine, silicon, or other non-carbon atoms.

Preferably, the substituted and unsubstituted hydrocarbon residues are selected from alkyl and aryl radicals which contain from about 1 to 30 carbon atoms or greater. More preferably, the alkyl radicals contain from 1 to 18 carbon atoms, while the aryl, arylalkyl, alkylaryl and cycloalkyl radicals preferably contain from 6 to 18 carbon atoms or greater.

In a preferred embodiment of this invention, R_1, R_2, R_7 and R_8 can individually be a hydrocarbon radical represented by the formula:

$$\begin{array}{l} R_{16}\text{-}(OCH_2)_h \\ \qquad\qquad\quad \backslash \\ \qquad\qquad\quad\; R_{18}\text{-} \\ \qquad\qquad\quad / \\ R_{17}\text{-}(OCH_2)_i \end{array} \qquad \text{(iii)}$$

wherein R_{16} and R_{17} are as defined for R_1, R_2, R_7 and R_8 above, h and i are the same or different and are a value of 0 or 1, and R_{18} is as defined for R_3 above. For compounds represented by formulae (i) and (ii), it is understood that each formula (iii) radical in a given compound may be the same or different and the R_{16} and/or R_{17} groups may themselves be a formula (iii) radical to provide complex hydrophobes of a dendritic or of a cascading nature as described below. Further, R_4, R_5, R_{10} and R_{13} can individually be a hydrocarbon radical represented by the formula:

$$-CH[(OR_{19})_jOR_{20}]- \qquad \text{(iv)}$$

wherein R_{19} is as defined for R_4, R_5, R_{10} and R_{13} above, R_{20} is as defined for R_6, R_{11} and R_{14} above, and j is a value of 0 or greater.

Illustrative ionic substituents for R_6, R_{11}, R_{14} and R_{20} include cationic and anionic substituents such as sulfates, sulfonates, phosphates, carboxyls and the like. R_6, R_{11}, R_{14} and R_{20} may preferably be an organic residue containing 1 or more hydroxyls or nitrogen derivatives or epoxides or other reactive groups which may or may not contain unsaturation.

Other illustrative terminal groups which are described by R_6, R_{11}, R_{14} and R_{20} include, for example, hydrocarbon residues which may contain allylic or vinylic unsaturation, acrylic or methacrylic functionality, styryl or alpha-methylstyryl functionality, and the like, such as the reaction product between the terminal alcohol (R_6, R_{11}, R_{14} and R_{20} = H) and glycidyl methacrylate, isocyanatoethyl methacrylate, alpha, alpha-dimethyl-m-isopropenyl benzyl isocyanate (m-TMI), and the like. Other examples of terminal groups may include hydrocarbon residues of alkyl, aryl, aralkyl, alkaryl, and cycloalkyl radicals which may or may not be substituted with one or more of the following: hydroxyl, carboxyl, isocyanato,

amino, mono- o or disubstituted amino, quaternary ammonium, sulfate, sulfonaate, phosphate, epoxy, and the like and may or may not contain other nnon-carbon atoms including silicon or fluorine. Also included can bee divalent siloxy radicals. Other nonhydrocarbon terminal grouppps may include sulfates, phosphates, and the like.

Illlustrative divalent hydrocarbon residues represented by R_3, R_4, R_5, RR_9, R_{10}, R_{12}, R_{13}, R_{15}, R_{18} and R_{19} in the above formulae includde substituted and unsubstituted radicals selected from alkylene, , -alkylene-oxy-alkylene-, -arylene-oxy-arylene-, arylene, alicycllic radicals, phenylene, naphthylene, -phenylene-$(CH_2)_m(Q)_n(CCH_2)_m$-phenylene- and -naphthylene-$(CH_2)_m(Q)_n(CCH_2)_m$-naphthylene- radicals, wherein Q individually represents a suubstituted or unsubstituted divalent bridging group selected from -$CCR_{21}R_{22}$-, -O-, -S-, -NR_{23}-, -$SiR_{24}R_{25}$- and -CO-, wherein R_{21} annd R_{22} individually represent a radical selected from hydrogen, alkyl/l of 1 to 12 carbon atoms, phenyl, tolyl and anisyl; R_{23}, R_{24} and R_{25} inndividually represent a radical selected from hydrogen and methyl, anod each m and n individually have a value of 0 or 1. More specific illllustrative divalent radicals represented by R_3, R_4, R_5, R_9, R_{10}, R_{12}, RR_{13}, R_{15}, R_{18} and R_{19} include, e.g., 1,1-methylene, 1,2-ethylene, 1,3-pnropylene, 1,6-hexylene, 1,8-octylene, 1,12-dodecylene, 1,4-phenylene, , 1,8-napthylene, 1,1'-biphenyl-2,2'-diyl, 1,1'-binaphthyl-2,2'-diyl, 2,2'-biinaphthyl-1,1'-diyl and the like. The alkylene radicals may contain frcom 2 to 12 carbon atoms or greater, while the arylene radicals may ccontain from 6 to 18 carbon atoms or greater. Preferably, R_3, , R_4, R_5, R_9, R_{10}, R_{12}, R_{13}, R_{15}, R_{18} and R_{19} are an alkylene or aryylene radical. The permissible divalent hydrocarbon residues may c contain fluorine, silicon, or other non-carbon atoms.

Illlustrative trivalent hydrocarbon residues represented by R_3, R_9, R_{12} and R_{18} in the above formulae incluode substituted and unsubstituted radicals selecteed from $>$CH-, $>$C(R_{26})-, $>$$CR_{27}$- and the

like, wherein R_{26} is a substituted or unsubstituted monovalent hydrocarbon residue as described herein and R_{27} is a substituted or unsubstituted divalent hydrocarbon residue as described herein.

Of course, it is to be further understood that the hydrocarbon residues in the above formulae may also be substituted with any permissible substituent. Illustrative substituents include radicals containing from 1 to 18 carbon atoms such as alkyl, aryl, aralkyl, alkaryl and cycloalkyl radicals; alkoxy radicals; silyl radicals such as $-Si(R_{28})_3$ and $-Si(OR_{28})_3$, amino radicals such as $-N(R_{28})_2$; acyl radicals such as $-C(O)R_{28}$; acyloxy radicals such as $-OC(O)R_{28}$; carbonyloxy radicals such as $-COOR_{28}$; amido radicals such as $-C(O)N(R_{28})_2$ and $-N(R_{28})COR_{28}$; sulfonyl radicals such as $-SO_2R_{28}$; sulfinyl radicals such as $-SO(R_{28})_2$; thionyl radicals such as $-SR_{28}$; phosphonyl radicals such as $-P(O)(R_{28})_2$; as well as halogen, nitro, cyano, trifluoromethyl and hydroxy radicals and the like, wherein each R_{28} can be a monovalent hydrocarbon radical such as alkyl, aryl, alkaryl, aralkyl and cycloalkyl radicals, with the provisos that in amino substituents such as $-N(R_{28})_2$, each R_{28} taken together can also compromise a divalent bridging group that forms a heterocyclic radical with the nitrogen atom, in amido substituents such as $-C(O)N(R_{28})_2$ and $-N(R_{28})COR_{28}$, each R_{28} bonded to N can also be hydrogen, and in phosphonyl substituents such as $-P(O)(R_{28})_2$, one R_{28} can by hydrogen. It is to be understood that each R_{28} group in a particular substituent may be the same or different. Such hydrocarbon substituent radicals could possibly in turn be substituted with a permissible substituent such as already herein outlined above.

Preferred alkylene oxides which can provide random or block oxyalkylene units in the complex hydrophobe compounds represented by formulae (i) and (ii) include alkylene oxides such as ethylene oxide, propylene oxide, 1,2-butylene oxide, 2,3-butylene oxide, 1,2- and 2,3-pentylene oxide, cyclohexylene oxide, 1,2-hexylene

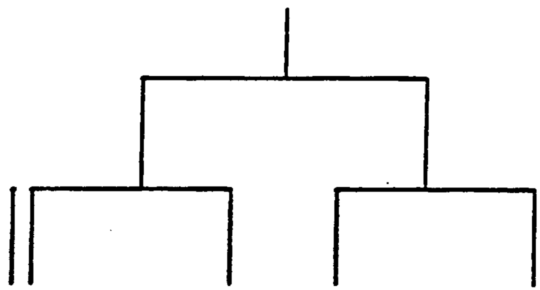
oxide, 1,2-octylene oxide, 1,2-decylene oxide, and higher alpha-olefin epoxides; epoxidized fatty alcohols such as epoxidized soybean fatty alcohols and epoxidized linseed fatty alcohols; aromatic epoxides such as styrene oxide and 2-methylstyrene oxide; and hydroxy- and halogen-substituted alkylene oxides such as glycidol, epichlorohydrin and epibromohydrin. The preferred alkylene oxides are ethylene oxide and propylene oxide. Also included can be hydrocarbon residues from substituted and unsubstituted cyclic esters or ethers such as oxetane and tetrahydrofuran. It is understood that the compounds represented by formulae (i) and (ii) herein can contain random and/or block oxyalkylene units as well as mixtures of oxyalkylene units. It is further understood that each R_4, R_5, R_{10}, R_{13} and R_{19} group in a particular substituent for all positive values of x, y, f, g and j respectively can be the same or different.

The values of x, y, z, f, g and j are not narrowly critical and can vary over a wide range. For example, the values of x, y, z, f, g and j can range from 0 to about 200 or greater, preferably from about 0 to about 100 or greater, and more preferably from about 0 to about 50 or greater. Any desired amount of alkylene oxide can be employed, for example, from 0 to about 90 weight percent or greater based on the weight of the complex hydrophobe compound.

Referring to the general formulae (i) and (ii) above, it is appreciated that when R_1, R_2, R_7 and/or R_8 are a hydrocarbon residue of formulae (iii) above, the resulting compound may include any permissible number and combination of hydrophobic groups of the dendritic or cascading type. Such compounds included in the above general formulae should be easily ascertainable by one skilled in the art.

In a preferred embodiment of this invention, the structure shown in formula (iii) can be a residue of the reaction product between epichlorohydrin and an alcohol, including those alcohols whose residues can be described by formula (iii), or a

phenolic, or a mixture thereof. The structures which result can be described as complex hydrophobes of a dendritic or of a cascading nature. Pictorially, they can be described as shown below:



Illustrative starter components useful for making the complex hydrophobe compounds of this invention include those compounds having active hydrogens such as alcohols (mono-, di- and polyhydric alcohols), phenols, carboxylic acids (mono-, di- and polyacids), and amines (primary and secondary). Frequently, the organic compounds contain up to about 100 or 150 carbons (in the case of polyol polymers) and can contain aliphatic and/or aromatic structures. Most often, the starter compounds are selected from the group of mono-, di- and trihydric alcohols having up to about 30 carbon atoms or greater. The organic compounds having active hydrogens can be the product of hydroformylation/hydrogenation reactions. Other useful starters can include the reaction products between epichlorohydrin and the above mentioned starter compounds.

PParticularly preferred starter alcohols are primary and secondary ı monohydric alcohols which are branched chain such as ethanol, proppanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanαol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hhexadecanol, octadecanol, isopropyl alcohol, 2-ethylhexanol, ssec-butanol, isobutanol, 2-pentanol, 3-pentanol and isodecanol. Panrticularly suitable alcohols are linear and branched primary alcohobls (including mixtures) such as produced by the "Oxo" reaction oof C_3 to C_{20} olefins. The alcohols may also be cycloaliphatic ssuch as cyclopentanol, cyclohexanol, cycloheptanol, cyclooctanol, ass well as aromatic substituted aliphatic alcohols such as benzyl alcohαol, phenylethyl alcohol, and phenylpropyl alcohol. Other aliphaticc structures include 2-methoxyethanol and the like.

PPhenols include alkylphenyls of up to 30 carbons such as phenol, methhylphenol, ethylphenol, butylphenol, heptylphenol, octylphenol, nonnylphenol, dinonylphenol and decylphenol. The aromatic radicaals may contain other substituents such as halide atoms.

AAlcohols (polyols) having 2 or more hydroxyl groups, e.g., about two tto six hydroxyl groups and have 2 to 30 carbons, include glycols s such as ethylene glycol, propylene glycol, butylene glycol, pentylenne glycol, hexylene glycol, neopentylene glycol, decylene glycol,l, diethylene glycol, triethylene glycol and dipropylene glycol. Other ppolyols include glycerine, 1,3-propanediol, pentaerythritol,l, galactitol, sorbitol, mannitol, erythritol, trimethylolethaane and trimethylolpropane.

TThe complex hydrophobe compounds can be prepared using a numberr of different methods. Three methods are described below, but synthhesis of these structures is not limited to just these methods.

TThe first method involves reaction of an unsubstituted or substituted aalcohol or phenol, such as nonylphenol for example,

with an epoxide-containing hydrocarbon residue, such as nonylphenol glycidyl ether. The reaction can be carried out under anhydrous conditions in the presence of at least 0.1 weight % but not more than 20 weight % of a suitable catalyst based on the starting weight of alcohol or phenol. Such a suitable catalyst can be, for example, potassium hydroxide. Use of a suitable azeotroping solvent, such as toluene or cyclohexane, can aid in removal of water from the system. The reaction temperature should be at least about 60°C and at most the boiling point of the solvent, unless the reaction is done under pressure. The reaction can be carried out under vacuum or in the absence of a solvent. The catalyst and the alcohol can be added to the solvent, and essentially all water can be removed, typically through azeotropping. Once the reaction temperature is reached, the epoxide can be added. The product can be isolated by removal of solvent. An example of this type of procedure for producing a complex hydrophobe is described in Example 1.

A second method involves reaction of a polymerizable cyclic ether, such as an epoxide, with a suitable polymerization catalyst like boron trifluoride in the presence of an initiating alcohol or phenol, referred to as the starter. The reaction can be done in a suitable polymerization solvent such as cyclohexane, which can be dried prior to polymerization/oligomerization through its azeotrope. The reaction can be carried out in the absence of a solvent. In a typical preparation, the catalyst, usually added at a level of from 0.1 mole % to 50 mole %, preferably from 0.1 mole % to 10 mole % based on the starting epoxide, and the starter, usually added at a level of from 5.0 mole % to 100 mole %, preferably from 5.0 mole % to 50 mole %, based on the starting epoxide, can be added to the solvent. The reaction temperature can be as low as -78°C to as high as the reflux temperature of the solvent at atmospheric pressure, but more preferably from 25°C to 75°C. The cyclic ether can then be added to the catalyst solution and polymerized. An example of this type of

procedure for producing a complex hydrophobe is described in Example 5.

A third method involves the reaction of an unsubstituted or substituted alcohol or phenol, such as nonylphenol or hexadecanol, , with a functional epoxide, such as epichlorohydrin. The starting alcohol or phenol can be added to a suitable reaction solvent, such as toluene, along with potassium hydroxide, a tetraalkyl ammonium halide, such as tetraethylammonium iodide, and water. The reaction can be carried out in the absence of a solvent. The reaction temperature can be regulated at about 65°C at which time the epichlorohydrin can be added. Varying the amount of epichlorohydrin and other ingredients can result in the formation of various dendritic-like molecules. An example of this type of procedure for producing a complex hydrophobe is described in Example 8.

The alkoxylation is conducted using a catalytically-effective amount of a catalyst, e.g., about 0.01 to 10, often about 0.5 to 5, weight percent based on the weight of a starter component, e.g., a complex hydrophobe compound having at least one active hydrogen. The catalysts should retain their activities during the alkoxylation, regardless of the amount of alkylene oxide employed. Thus, the amount of catalyst can be based on the amount of starter provided to the alkoxylation zone and not the degree of alkoxylation to be effected.

Illustrative alkoxylation catalysts useful in this invention include, for example, potassium hydroxide, diethylaluminum fluoride, oxides and hydroxides of barium and strontium, basic salts of alkaline earth metals especially calcium, calcium oxide (quicklime), calcium hydroxide (slaked line), calcium sulfate, and the like. Preferred catalysts for obtaining alkoxylation product mixtures having a narrow molecular weight distribution are disclosed in U.S. Patent 4,754,075, the disclosure of which is

incorporated herein by reference. This invention is not intended to be limited in any manner by the permissible catalysts.

Normally, the catalyst and the starter component are admixed and then the alkylene oxide is added at the reaction temperature until the desired amount of alkylene oxide has been added, then the product is neutralized and can be finished, if desired, in any procedure including stripping unreacted starter material from the product mixture, filtration, or further reaction.

The temperature of the alkoxylation is sufficient to provide a suitable rate of reaction and without degradation of the reactants or reaction products. Often, the temperatures range from between about 50°C and 270°C, e.g. from about 100°C to 200°C. The pressure may also vary widely, but when low-boiling alkylene oxides such as ethylene oxide and propylene oxide are employed, a pressurized reactor is preferably used.

The alkoxylation reaction medium is preferably agitated to ensure a good dispersal of the reactants and catalyst throughout the reaction medium. Also, the alkylene oxide is usually added at a rate approximating that which it can be reacted.

Neutralization may assist in the recovery of the catalyst from the alkoxylation product mixture. When neutralizing, acids that may tend to form catalyst-containing gel structures or solids that clog filtering apparatus should be avoided. Conveniently, sulfuric acid, phosphoric acid, propionic acid, benzoic acid and the like are used.

The above procedure represents but one of many equally viable versions of suitable alkoxylation processes. Other versions are possible through combinations of the options available in the various process steps.

The catalytic alkoxylation reactions of this invention can be effected, for example, by conventional methods such as (1) batch processes; (2) continuous fixed-bed processes; and (3)

continuous fluiddized reactor processes. In a batch reactor, the catalyst is kept t suspended in the reactant by shaking or stirring. In a fluidized reaccctor, the catalyst is at a particular original level. As the velocity of tlthe reactant stream is increased, the catalyst bed expands upwarrd to a second level, and at a critical velocity it enters into violent turlrbulence. The fluidized reactor is particularly useful for removing orr supplying the heat necessary to maintain a fixed catalyst temperrature. The fluidized reactor can usually be employed only on a ratheer large scale since good fluidization requires a reactor larger than abo͏out 1.5 inches in diameter.

AAs indicated above, the end groups described by R_6, R_{11}, R_{14} and RR_{20} can be a variety of structures including sulfates. The sulfation otbf a hydroxyl containing end group can be carried out using one of seeveral methods, such as with SO_3 or sulfamic acid.

IIn the sulfation reaction using sulfamic acid, a complex hydropphobe alkoxylate, for example ethoxylated 1,3-bis(nonylphenoxxy)-2-propanol, is dried at high temperature, at or about 100°C fonr example, and low pressure, at or below 50 mm Hg for example. The e ethoxylate is cooled to a reaction temperature at or about 60°C, forr example, and sulfamic acid is charged. The reaction temperature is kept at or about 110°C. Once the reaction is complete, an amount of aa mono- or disubstituted alkanolamine can be added to remove residuaal acid, and prevent hydrolysis upon introduction of water. A dilutiting solvent, such as ethanol and/or water, can be added along wiith the alkanolamine. An example of a preparation of a sulfate usingg sulfamic acid is shown in Example 11.

The alkoxylation products produced by the alkoxylation proccesses of thiis invention, including the complex hydrophobe compounds havving at least one active hydrogen, can undergo further reaction(s) to aafford desired derivatives thereof. Such permissible derivatization reactions can be carried out in accordance with conventional pprocedures known in the art. Illustrative derivatization

reactions include, for example, esterification, etherification, amination, alkylation, hydrogenation, dehydrogenation, reduction, acylation, condensation, carboxylation, oxidation, silylation and the like, including permissible combinations thereof. This invention is not intended to be limited in any manner by the permissible derivatization reactions or permissible derivatives of alkoxylation products and complex hydrophobe compounds.

More particularly, the hydroxyl-terminated alkoxylation products and complex hydrophobe compounds of this invention can undergo any of the known reactions of hydroxyl groups illustrative of which are reactions with acyl halides to form esters; with ammonia, a nitrile, or hydrogen cyanide to form amines; with alkyl acid sulfates to form disulfates; with carboxylic acids and acid anhydrides to form esters and polyesters; with alkali metals to form salts; with ketenes to form esters; with acid anhydrides to form carboxylic acids; with oxygen to form aldehydes and carboxylic acids; ring-opening reactions with lactones, tetrahydrofuran; dehydrogenation to form aldehydes, isocyanates to form urethanes, and the like.

Alkoxylation product mixtures prepared by the processes of this invention comprise alkoxylation species that can be represented by the formulae (i) and/or (ii) above. The alkoxylation product mixtures of this invention can be characterized as the condensation reaction products of alkylene oxides and complex hydrophobe compounds having at least one active hydrogen in which the mole ratio of reacted alkylene oxide per active hydrogen is at least about 4, say, about 4 to 16 or 24, preferably about 5 to 12. The product mixtures can have at least one alkoxylation moiety which constitutes at least about 10, say, about 20 to 30 or 40, and most often about 20 to 30, weight percent of the composition. The alkoxylation mixtures of this invention also can have a relatively symmetrical distribution. Hence, the portion of the product mixture having three or more

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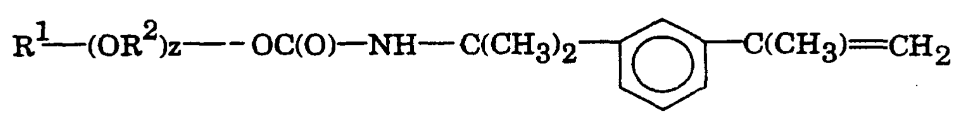
oxyalkylene unit groups (per active hydrogen site of the complex hydrophobe compound) than the peak alkoxylation specie is relatively minor, e.g., often less than about 12, say, less than 10, and often about 1 to 10, weight percent of the mixture. Similarly, the alkoxylation species having fewer oxyalkylene groups (per active hydrogen site of the complex hydrophobe compound) by three or more oxyalkylene groups from the average peak alkoxylation species is usually relatively minor, e.g., less than about 15, say, less than about 10, often about 0.5 to 10, weight percent of the composition. Generally, the one oxyalkylene unit higher and the one oxyalkylene unit lower alkoxylates in respect to the most prevalent alkoxylation specie are present in a weight ratio to the most prevalent alkoxylation specie of about 0.6:1 to 1:1.

The nonionic surfactant compounds encompassed by formulae (i) and (I) may be converted to anionic surfactant compounds by chemically modifying a terminal or pendant hydroxyl group thereof. One such approach includes the steps of reacting the nonionic surfactant compounds encompassed by formulae (i) and (I) with sulfuric acid or sulfamic acid and then optionally converting the resulting free sulfate esters (when sulfuric acid is used) or ammonium salts (when sulfamic acid is used) into corresponding alkali metal or alkanolamine salts such as monoethanolamine by conventional procedures.

Another approach includes the steps of reacting the nonionic surfactant compounds encompassed by formulae (i) and (I) with phosphorus pentoxide or phosphorus oxychloride and then optionally converting the resulting free phosphate esters into corresponding salts with alkali metal, ammonium or alkanolamine salts whereby mixtures of mono-esters and di-esters are obtained. These mixtures may be used as an anionic surfactant without being isolated into their constituents.

A fufurther approach includes the steps of reacting the nonionic surfactstant compounds encompassed by formulae (i) and (I) with maleic anhhydride, reacting resultant maleate esters with an alkali metal bisuulfite and then optionally converting the resulting alkali metal sulflfosuccinates into corresponding free acids or ammonium or alilkanolamine salts. When at least one mole of maleic anhydride is useed relative one mole of the compounds of the formula (i) and (I) in thee above reaction, mixtures of half ester isomers having a sulfo group attatached to either alpha or beta position relative to the terminal carboxyyl group. These mixtures may also be used as an anionic surfactaant without isolation. Conversely, when at least two moles of the commpounds of the formulae (i) and (I) are reacted with one mole of maldeic anhydride, di-esters are obtained.

Preeferred macromonomer compounds useful in this invention includde those represented by the formulae:



(XII)

$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\qquad\quad R^4 \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ R^1\text{-}(OR^2)_z\text{-}CH_2CCHCH_2OCH_2C{=}CH_2 \\ \qquad\qquad\quad || \\ \qquad\qquad((OR_{19})_jOH \end{array} \qquad (XIII)$$

$$R^1 - (OR^2)_z - OCC(O)-C(R^4)=CH_2 \qquad (XIV)$$

wherein R^1, $R^2$2, R^4, R_{19}, z and j are as defined herein.

Thhe macromonomer compounds useful in this invention can undergo fuurther reaction(s) to afford desired derivatives thereof. Such permissibble derivatization reactions can be carried out in accordance witlth conventional procedures known in the art. Illustrative derrivatization reactions include, for example, esterification, eetherification, alkoxylation, amination, alkylation, hydrogenation,ι, dehydrogenation, reduction, acylation, condensation, carboxylation, c oxidation, silylation and the like, including permissible conmbinations thereof. In an embodiment of this invention, the ı macromonomers can contain carboxyl or other ionic or acid moieties. 7This invention is not intended to be limited in any manner by the ɜ permissible derivatization reactions or permissible derivatives of ı macromonomer compounds.

Mdore particularly, the hydroxyl-terminated macromonomerr compounds of this invention can undergo any of the known reactionns of hydroxyl groups illustrative of which are reactions with ı acyl halides to form esters; with ammonia, a nitrile, or hydrogen cyyanide to form amines; with alkyl acid sulfates to form disulfates; withh carboxylic acids and acid anhydrides to form esters and polyesters;;; with alkali metals to form salts; with ketenes to form esters; with acicid anhydrides to form carboxylic acids; with oxygen to form aldehydess and carboxylic acids; ring-opening reactions with lactones, tetrahhydrofuran; dehydrogenation to form aldehydes, isocyanates to f form urethanes, and the like.

Thhe monoethylenically unsaturated macromonomer component is ssubject to considerably variation within the formula presented previiously. The essence of the maromonomer is a complex

hydrophobe carrying a polyethoxylate chain (which may include some polypropoxylate groups) and which is terminated with at least one hydroxy group. When the hydroxy-terminated polyethoxylate complex hydrophobe used herein is reacted with a monoethylenically unsaturated monoisocyanate, for example, the result is a monoethylenically unsaturated urethane in which a complex hydrophobe polyethoxylate structure is associated with a copolymerizable monoethylenic group via a urethane linkage.

The monoethylenically unsaturated compound used to provide the monoethylenically unsaturated macromonomer is subject to wide variation. Any copolymerizable unsaturation may be employed, such as acrylate and methacrylate unsaturation. One may also use allylic unsaturation, as provided by allyl alcohol. These, preferably in the form of a hydroxy-functional derivative, as is obtained by reacting a C_2-C_4 monoepoxide, like ethylene oxide, propylene oxide or butylene oxide, with acrylic or methacrylic acid to form an hydroxy ester, are reacted in equimolar proportions with an organic compound, such as toluene diisocyanate or isophorone diisocyanate. The preferred monoethylenic monoisocyanate is styryl, as in alpha, alpha-dimethyl-m-isopropenyl benzyl isocyanate. Other suitable organic compounds include, for example, monoethylenically unsaturated esters, ethers, amides, ureas, anhydrides, other urethanes and the like.

The polymers of this invention can be prepared via a variety of polymerization techniques known to those skilled in the art. The technique of polymerization influences the microstructure, monomer sequence distribution in the polymer backbone and its molecular weight to influence the performance of the polymer. Illustrative polymerization techniques include, for example, conventional and staged emulsion polymerization via batch, semi-continuous, or continuous processes, micellar polymerization, inverse emulsion polymerization, solution polymerization, non-

aqueous dispersion polymerization, interfacial polymerization, emulsion polymerization, suspension polymerization, precipitation polymerization, addition polymerizations such as free radical, anionic, cationic or metal coordination methods, and the like.

The thickeners of this invention possess structural attributes of two entirely different types of thickeners (those which thicken by pH dependent solubilization, e.g., alkali solubilization, of a high molecular weight entity, and those which thicken due to association), and this may account for the superior thickener properties which are obtained herein.

The aqueous emulsion copolymerization is entirely conventional. To obtain an estimate of thickening efficiency, the product can be diluted with water to about 1% solids content and then adjust the pH to solubilize the polymer or neutralized with alkali. The usual alkali is ammonium hydroxide, but sodium and potassium hydroxide, and even amines, like triethylamine, may be used for neutralization. The usual acid is sulfuric acid, acetic acid and the like. After neutralization or adjustment to appropriate pH, the product dissolves in the water to provide an increase in the viscosity. In the normal mode of addition, the unsolubilized or unneutralized thickener is added to a paint and then the pH is adjusted or neutralized. This facilitates handling the thickener because it has a lower viscosity before pH adjustment or neutralization. This procedure also makes more water available for the paint formulation.

The polymers of this invention are preferably produced by conventional aqueous emulsion polymerization techniques, using appropriate emulsifiers for emulsifying the monomers and for maintaining the polymer obtained in a suitable, dispersed condition. Commonly used anionic surfactants such as sodium lauryl sulfate, dodecylbenzene sulfonate and ethoxylated fatty alcohol sulfate can be

used as emulsifiers. The emulsifier may be used in a proportion of 1/2 to 6% of the weight monomers.

Preeferably, water-soluble initiators such as alkali metal or ammonium ppersulfate are used in amounts from 0.01 to 1.0% on the weight of mnonomers. A gradual addition thermal process employed at tenmperatures between 60°C to 100°C is preferred over redox systems.

Thae polymerization system may contain small amounts (0.01 to 5% by wweight, based on monomer weight) of the chain transfer agent mercaptans such as hydroxyethyl mercaptan, ß-mercaptopropiopnic acid and alkyl mercaptans containing from about 4 to 22 carbon aatoms, e.g., ethyl hexyl mercapto propionate and tertiary dodecyl mercaptan, and the like. The use of mercaptan modifier reducees the molecular weight of the polymer and therefore its thickening eefficiency.

Thae polymers of this invention may further be modified by introducing an amount of component (D), namely, one or more polyethylenicallly unsaturated copolymerizable monomers effective for crosslinkingg, such as diallylphthalate, divinylbenzene, allyl methacrylate, tritrimethylol propane triacrylate, ethyleneglycol diacrylate or diimethacrylate, 1,6-hexanediol diacrylate or dimethylacrylatte, diallyl benzene, and the like. Thus, from about 0.05 or less to abbout 20% or greater of such polyethylenically unsaturated conmpound based on total weight of monomer may be included in the composition forming the polymer. The resulting polymers are eitither highly branched or in the form of three-dimensional nettworks. In the neutralized salt form, those networks swell in an aquaeous system to act as a highly efficient thickener.

Otther illustrative polyethylenically unsaturated monomers usefful in this invention include, for example, any copolymerizablele compound which contains two or more nonconjugated points of ethylenic unsaturation or two or more

nonconjugated vinylidene groups of the structure, CH_2=C=, such as divinyltoluene, , trivinylbenzene, divinylnaphthalene, trimethylene glycol diacrylatte or dimethacrylate, 2-ethylhexane-1,3-dimethyacrylatte, divinylxylene, divinylethylbenzene, divinyl ether, divinyl sulfone,, allyl ethers of polyhdric compounds such as of glycerol, pentaaerythritol, sorbitol, sucrose and resorcinol, divinylketone, divinylsulfide, allyl acrylate, diallyl maleate, diallyl fumarate, diallyl phthalate, diallyl succinate, diallyl carbonate, diallyl malonatte, diallyl oxalate, diallyl adipate, diallyl sebacate, diallyl tartrate,, diallyl silicate, triallyl tricarballylate, triallyl aconitate, triallllyl citrate, triallyl phosphate, N,N-methylenediacrrylamide, N,N'-methylenedimethacrylamide, N,N'-ethylidenediacrrylamide and 1,2-di-(a-methylmethylenesulfonamide)-ethylene.

Thhe polymer may be utilized in a variety of ways to provide the thiickener or thickened compositions of this invention. For example, tthe polymer, while in aqueous dispersion or dry form, may be blendedd into an aqueous system to be thickened followed by addition of a pbH adjusting agent, e.g., neutralizing agent. Alternatively, the polymer may first be solubilized or neutralized in aqueous disperrsion form and then blended with the aqueous system. Preferably, if ccо-thickening by a surfactant is desired, the components aree separately blended (as dry components or as dispersions or slurries) into an aqueous dispersion to be thickened, followed by thee pH adjustment step, e.g., neutralization step. Although aqueeous concentrates of the polymer in unsolubilized form, e.g., in acid forrm, and the surfactant may be formed and added to an aqueous disperrsion to be thickened as needed, followed by pH adjustment, e.g.g., neutralization, such concentrates tend to be too viscous for easyy handling. It is nevertheless possible to prepare either a dry bldend or an aqueous, high solids composition which is sufficiently loww in viscosity as to be pumpable or pourable, and then to

further thicken the admixture by addition of alkaline or acidic materials.

The polymer thickener may be provided in a dry state in number of ways. For example, the unsolubilized polymer may be spray or drum dried and, if desired, blended with a surfactant co-thickener. However, it is also possible to spray dry or otherwise dehydrate the solubilized polymer thickener, and then reconstitute the aqueous thickener dispersion at a future time and place by agitation in a aqueous medium, provided the pH of the dispersion is maintained at an appropriate value, e.g., at pH 7 or higher for neutralization.

The more usual method of application of the dispersion of this invention for aqueous thickening is to add the aqueous dispersion of the polymer to the medium to be thickened and, after mixing, to introduce an alkaline or acidic material to ionize component (A). The major portion of the thickening effect is usually obtained in a few minutes upon pH adjustment. In the presence of high concentrations of electrolytes, the viscosity development may take much longer. This method of applying a polymer to an aqueous system before pH adjustment enables one to handle a high solids thickener in a non-viscous state, to obtain uniform blend, and then to convert to a highly viscous condition by the simple addition of an alkaline or acidic material to bring the pH of the system to an appropriate value.

The aqueous solutions thickened with the neutralized polymers of this invention exhibit good viscosity stability even at a pH as high as 13. The polymer may be used to thicken compositions under acidic conditions in the presence of a relatively large amount of surfactants wherein the thickened composition, for example, an aqueous system, has a pH below 7, even as low as 1.

An enhancement of thickening (herein termed "co-thickening") can result upon the addition of a surfactant to an

aqueous systemm containing the polymer of this invention, when the polymer is soluhbilized. In some cases the thickening can be enhanced up to o about 40 times the viscosity afforded by the solubilized polymer alone. . A wide range of surfactants may be used. Although trace amounts (of surfactant may be residually present from the polymerization ı of the monomers comprising the polymer (for example, whateever may remain of the about 1.5 weight percent surfactant on nmonomers), such amounts of surfactant are not believed to resuult in any measurable co-thickening.

Onn the basis of an aqueous system containing about 0.1 to 5% by weightt of polymer solids, a useful amount of surfactant for optimum co-thiickening is about 0.1 to 1.0% by weight of the total system. As inddicated, the amounts of polymer and surfactant cothickener maay vary widely, even outside these ranges, depending on polymer andd surfactant type and other components of the aqueous system to be thhickened. However, the co-thickening can reach a maximum as ssurfactant is added and then decreases as more surfactant is addded. Hence, it may be uneconomical to employ surfactant in anmounts outside the stated concentrations and polymer/surfacttant ratios, but this can be determined in a routine manner in eachh case.

Thhe preferred method of application of the polymer and the surfactant f for aqueous thickening is to add in any sequence the polymer and thhe surfactant to the medium to be thickened and, after mixing, to introoduce an alkaline or acidic material to adjust the pH. This method of f applying polymer and surfactant to an aqueous system before ppH adjustment enables one to handle a high solids thickener in a r non-viscous state, to obtain a uniform blend, and then to convert to a l highly viscous condition by the simple addition of an alkaline or aciddic material to bring the pH of the system to an appropriate valdue. However, the pH of the aqueous system may also be adjusted beffore addition of the surfactant.

Thee surfactants which may be used include nonionics and anionics, siringly or in combination, the selection necessarily depending upon ι compatibility with other ingredients of the thickened or thickenable dilispersions of this invention. Cationic and amphoteric surfafactants may also be used provided they are compatible with ι the polymer and other ingredients of the aqueous system, or are uused in such small amounts as not to cause incompatibility. .

Suititable anionic surfactants that may be used include the higher fatty r alcohol sulfates such as the sodium or potassium salt of the sulfates of f alcohols having from 8 to 18 carbon atoms, alkali metal salts or ammine salts of high fatty acid having 8 to 18 carbon atoms, and sulfoonated alkyl aryl compounds such as sodium dodecyl benzene sulfonatte. Examples of nonionic surfactants include alkylphenoxypolyyethoxyethanols having alkyl groups of about 7 to 18 carbon atoms anod about 9 to 40 or more oxyethylene units such as octylphenoxy-polylyethoxyethanols, dodecylphenoxypolyethoxy-ethanols; ethylenne oxide derivatives of long-chain carboxylic acids, such as lauric, mmyristic, palmitic, oleic; ethylene oxide condensates of long-chain alcocohols such as lauryl or cetyl alcohol, and the like.

Exaamples of cationic surfactants include lauryl pyridinium chlonride, octylbenzyltrimethyl-ammonium chloride, dodecyltrimethylylammonium chloride condensates of primary fatty amines and ethyylene oxide, and the like.

Thee foregoing and numerous other useful nonionic, anionic, cationic,c, and amphoteric surfactants are described in the literature, such ε as McCutcheon's Detergents & Emulsifiers 1981 Annual, North AAmerica Edition, MC Publishing Company, Glen Rock, NJ 074522, U.S.A., incorporated herein by reference.

In ggeneral, solvents and non-solvents (or mixtures of solvents, non-sollvents other organics and volatiles) can be used to manipulate the vviscosity of polymer containing systems. In the

examples hereiin, it is interesting to note how mineral spirits act like co-thickener, annd how the water solubility of the other solvent influences how v much mineral spirits can be added before the solution separaates into a two phase system. The co-thickening with mineral spirits s has utility in textile printing pastes, and in waterborne autitomotive basecoats. These systems usually contain mineral spirits s (because of the pigments used therein), so that the mineral spirits s provide an economical way of increasing viscosity and improving ; the efficiency of the thickener.

Thhe amount of the polymer that may be dissolved in any given aqueous ‹ composition may fall within a wide range depending on the particuldar viscosity desired.

Thhus, although any effective amount of the polymer may be employed fonr dissolution, typically from about 0.05 to about 20%, preferably fromn about 0.1 to about 5%, and most preferably from about 0.1 to about 3%% by weight, based on the weight of the final aqueous composition inacluding polymer is used.

Foor latex paint compositions, the polymer may be dissolved thereiin in an amount of from about 0.05 to about 5%, and preferably fromn about 0.1 to about 3% by weight, based on the weight of the total conmposition including polymer.

Thhe polymers of this invention may be employed as thickeners for c controlling viscosity of any aqueous based composition. An aqueous baased composition is an aqueous composition as herein defined to be a ι composition wherein water comprises at least 10% by weight of the tdotal composition (including 100% water).

Foor example, aqueous dispersions, emulsions, suspensions, soolutions, slurries and the like, may be thickened by the polymers of thiis invention.

Tyypical aqueous compositions include compositions to be applied to textiiles such as latex adhesives, warp sizes, backings for rugs and other r pile fabrics. The polymer may also be used when

thickening is deesired in the purification of raw water such as the saline water useed in the recovery of oil from exhausted oil wells by water flooding tdechniques. Other aqueous coatings compositions to which the polymmer can be added for thickening purposes include drilling muds, cxaulks, adhesives, coating compositions such as paper coatings, 1 furniture finishes, ink compositions, latex paints, foundary core wvashes, and the like.

Prebferably, the polymer is used to thicken aqueous coating compositions, and more preferably latex paint compositions. Examples of suititable latex paint compositions include those based on resins or bindersrs of acrylonitrile, copolymers of acrylonitrile wherein the comonomer i is a diene like isoprene, butadiene or chloroprene, homopolymers obf styrene, homopolymers and copolymers of vinyl halide resins suach as vinyl chloride, vinylidene chloride or vinyl esters such as viinyl acetate, vinyl acetate homopolymers and copolymers, copoolymers of styrene and unsaturated acid anydrides like maleic anhyydrides, homopolymers and copolymers of acrylic and methacrylic acidd and their esters and derivatives, polybutadiene, polyisoprene, buutyl rubber, natural rubber, ethylene-propylene copolymers, olefifins resins like polyethylene and polypropylene, polyvinyl alcohobl, carboxylated natural and synthetic latices, epoxies, epoxy esters andd similar polymeric latex materials.

Latdtex paint compositions are well known in the art and typically compririse an emulsion, dispersion or suspension of discrete particles of resinn binder and pigment in water. Optional ingedients typicaly include ɜ thickeners, antifoam agents, plasticizers, surfactants, coaklescing agents, and the like.

Thee polymers described herein are useful in a variety of aqueous systemss, such as textile coatings (woven and nonwoven), latex paint formnulations, cosmetic formulations, pigment dispersions and 1 slurries, dentrifrices, hand lotions, liquid detergents, quenchants, agricultural chemicals, concrete additives,

transmission fldluids, waste water treatment (flocculants), turbulent drag reduction,ı, aircraft anti-icing, automation coatings (OEM and refinish), architectural coatings, industrial coatings and the like.

Otther applications include, for example, paper making, mineral processsing, brine viscosification, superabsorbency, enhanced oil reecovery, personal care products, biomedical, pharmaceuticald and the like.

TThe macromonomers of this invention are particularly useful as an emmulsifier in the emulsion or dispersion polymerization of ethylenicallyy unsaturated monomers. Examples of monomers include acrylic : monomers such as acrylic acid, methyl acrylate, butyl acrylate, 2 ethylhexyl acrylate, methyl methacrylate, acrylonitrile, aacrylamide and 2-hydroxethyl acrylate; aromatic monomers suchh as styrene and divinylbenzene; vinyl esters such as vinyl acetate; hhalogen-containing monomers such as vinyl chloride and vinylidene chloride; conjugated diene monomers such as butadiene, isopprene and chloroprene; ethylene, maleic anhydride and methyl mahleate.

AAny known initiator such as hydrogen peroxide, potassium persulfate, azobisisobutyronitrile and benzoyl peroxide may be used in the emulsion polymerization in combination with a known polymerirization promoter such as sodium bisulfite and ammonium ferrous sulfate.

TThe macromonomers of this invention may be used in an amount of 0.1 to 20%, preferably 0.2 to 5.0% by weight of the total monomers singly or in combination with a conventional emulsifiers or protective colloid.

TThe resulting polymer emulsions or dispersion may be applied to woodds, metals, paper, textiles, and concrete structures as an adhesive, coating agent or reinforcing agent.

TThe macromonomer compounds of this invention find use not only as an emulsifier or dispersant of various materials such

as monomers in the emulsion or suspension polymerization, waxes, dyes, pigments and pesticides, but also as latex binders and as post-treating agents for textile materials and antistatic agents for plastic products. By the use of the macromonomers of this invention, defects of conventional surfactants remaining after use may be alleviated.

The macromonomer compounds of this invention can be homopolymerized or copolymerized with conventional monomers via a variety of polymerization techniques known to those skilled in the art. The technique of polymerization influences the microstructure, monomer sequence distribution in the polymer backbone and its molecular weight to influence the performance of the polymer. Illustrative polymerization techniques include, for example, conventional and staged emulsion polymerization via batch, semi-continuous, or continuous processes, inverse emulsion polymerization, solution polymerization, non-aqueous dispersion polymerization, interfacial polymerization, emulsion polymerization, suspension polymerization, precipitation polymerization, addition polymerizations such as free radical, anionic, cationic or metal coordination methods, and the like.

The surfactant compounds of this invention can be used wherever there is a need to increase surface activity. They are particularly valuable where process conditions demand the greatest efficiency from water, e.g., in wetting, penetrating, emulsifying, lubricating and dispersing. Illustrative applications include, for example, agriculture, e.g., emulsifiers and wetters, herbicidal adjuvants and fruit washes; cleaners, e.g., household detergents, dry cleaning detergents, industrial hand cleaners, detergent/sanitizers, solvent degreasers, metal cleaners, hard surface cleaners, commercial laundry detergents and car wash detergents; dust wetting, e.g., coal mines, ceramic industries and foundries; leather, e.g., hidesoaking, degreasing, fatliquor stabilization, tanning and dyeing; paint, e.g., emulsion polymerization of latexes, latex

stabilization, pi?igment wetting and dispersion; paper, e.g., pulping, absorbent papeers, de-inking waste water, wet-felt washing and adhesives; and textiles, e.g., greige goods scouring, bleaching, carbonizing of wwool, scouring of cotton, wool and polyester/cotton blends, wetting and rewetting agents, desizing of cotton and polyester/cottonn blends, polyethylene softener emulsifiers, mineral oil and solvent emnulsifiers, fiber lubricant emulsifiers, emulsion polymerization,, dyeing and finishing of synthetics, naturals and blends, dye leveleling agents and resin bath additives.

Addditionally, the compounds of this invention may be useful as compoonents of sanitizing solutions for use on food processing equipipment and utensils and on beverage containers, including milk containers and equipment; emulsifiers and/or surface active aagents in the manufacture of articles or components of articles intendeed for use in producing, manufacturing, packing, processing, prepparing, treating, packaging, transporting or holding food; inert (or oeccasionally active) ingredients for use in formulations applied to growiving crops or to raw agricultural commodities after harvest; and ineert (or occassionally active) ingredients for use in formulations appplied to animals.

As used herein, the term "complex hydrophobe" is contemplated tooo include all permissible hydrocarbon compounds having 2 or monre hydrophobe groups, e.g., bis-dodecylphenyl, bis-nonylphenyl, bisis-octylphenyl and the like.

Fonr purposes of this invention, the term "hydrocarbon" is contemplatedd to include all permissible compounds having at least one hydrogen annd one carbon atom. In a broad aspect, the permissible hyddrocarbons include acyclic and cyclic, branched and unbranched, caarbocyclic and heterocyclic, aromatic and nonaromatic orgganic compounds which can be substituted or unsubstituted.

As uused herein, the term "substituted" is contemplated to include all peermissible substituents of organic compounds unless otherwise indicatted. In a broad aspect, the permissible substituents include acyclic aand cyclic, branched and unbranched, carbocyclic and heterocyclic,:, aromatic and nonaromatic substituents of organic compounds. Illuustrative substituents include, for example, alkyl, alkyloxy, aryl, anryloxy, hydroxy, hydroxyalkyl, amino, aminoalkyl, halogen and the like in which the number of carbons can range from 1 to about 20 or nmore, preferably from 1 to about 12. The permissible substituents can be one or more and the same or different for appropriate orgaanic compounds. This invention is not intended to be limited in any maanner by the permissible substituents of organic compounds.

The invention is illustrated by certain of the following examples.

Example 1

Preparration of 1,3-Bis(nonylphenoxy)-2-propanol

To aa five neck, two liter round bottom flask equipped with an addition funnnel, thermometer, nitrogen dispersant tube, mechanical stirrrer, and a decanting head with a water-cooled condenser were aadded 220 grams (1.00 mole) of nonylphenol and 250 milliliters of cycldohexane. The solution was then heated to reflux and 2.8 grams (11.3 wt. % based on nonylphenol) of potassium hydroxide in 10 nmilliliters of water was slowly added to the flask. After essentially all the water was recovered in the decanting head (10 milliliters + 11 milliliter formed), 250.7 grams (0.91 mole) of nonylphenyl glyccidyl ether as added dropwise. During the addition of the glycidyl etheer, the reaction temperature was maintained between 60 and 80°C. Afifter the addition was complete, the solution was refluxed for four hours. The contents of the flask were then washed with a five perceent aqueous solution of phosphoric acid, and the

organic layer was separated from the water layer and washed twice with deionized water. The reaction mixture was then placed in a one liter round bottom flask, and the remaining cyclohexane and unreacted nonylphenol were recovered by distillation, first at atmospheric pressure, then under vacuum at 0.2 mm Hg. The kettle temperature was not allowed to exceed 180°C during the distillation to prevent discoloration of the product. The concentrated solution was then refiltered to give 425 grams of a pale-yellow liquid. End-group MW analysis gave a molecular weight of 506.8 (theoretical MW = 496.8). Ir and nmr spectra were identical to previously recorded spectra for the compound.

Example 2

Preparation of 1,3-Bis(nonylphenoxy)-2-propanol

To a five neck, two liter round bottom flask, equipped with an addition funnel, thermometer, nitrogen dispersant tube, mechanical stirrer, and a decanting head with a water-cooled condenser, were added 300 milliliters of cyclohexane and 451.7 grams (2.05 mole) of nonylphenol. The solution was then heated to reflux and 58.9 grams (1.05 mole) of potassium hydroxide in 60 milliliters of water was slowly added via the addition funnel. After essentially all the water was recovered in the decanting head (60 milliliter + 19 milliliters formed), the reaction was cooled to 40°C, and 92.5 grams (1.00 mole) of epichlorohydrin was slowly added. During the addition, the reaction temperature was maintained below 60°C by controlling the rate of epichlorohydrin addition. After all the epichlorohydrin was added, the solution was allowed to stir for one hour, and then brought to reflux for an additional three hours. The reaction mixture was then filtered under vacuum through a steam-jacketed Buchner funnel to remove the potassium chloride formed as a by-product. The filtration process was performed a total of three times to remove the majority of the salts. The reaction mixture was

then placed in a (one liter round bottom flask, and the remaining cyclohexane and (unreacted nonylphenol were recovered by distillation, first ; at atmospheric pressure, then under vacuum at 0.2 mm Hg. The ketttle temperature was not allowed to exceed 180°C during the distilldlation to prevent discoloration of the product. The concentrated soluution was then refiltered to give 275 grams of a pale-yellow liquid. Ernd-group MW analysis gave a molecular weight of 459.7 (theoreticall MW = 496.8). Ir and nmr spectra were identical to previously recordded spectra for the compound.

<u>Example 3</u>

<u>PPreparation of 5 Mole Ethoxylate of 1,3-Bis(nonylphenoxy)-2-propanol</u>

To aa 500 milliliter, stainless steel, high pressure autoclave was chnarged 200 grams (0.40 mole) of 1,3-bis(nonylphenoxyy)-2-propanol, which contained a catalytic amount of the potassium sahlt of the alcohol as described in Example 1. After purging the reacttor with nitrogen, the alcohol was heated to 130°C with stirring, andd 86.9 grams (2.0 mole) of ethylene oxide was added over a two hour ; period. The reaction temperature and pressure were maintained from 1 130°C to 140°C and 60 psig during the course of the reaction. After tthe addition of ethylene oxide was complete, the reaction mixture e was held at 140°C for an additional hour to allow all the ethylene oxidde to cook out. The reaction mixture was dumped while hot, under r nitrogen, and neutralized with acetic acid to yield 285 grams of a ppale-yellow liquid.

Example 4
Preparation of Adduct of Nonylphenyl Glycidyl Ether and 5 Mole Ethoxylate of 1,3-Bis(nonylphenoxy)-2-propanol

To a five neck, one liter, round bottom flask equipped as in Example 1 was added 119.8 grams (0.17 mole) of the 5 mole ethoxylate of 1,3,3-bis(nonylphenoxy)-2-propanol and 100 milliliters of cyclohexane. The mixture was refluxed (100°C) for one hour to remove residual water, and then cooled to 50°C under nitrogen to add 0.5 grams of BF_3/Et_2O. Nonylphenyl glycidyl ether (46.0 grams, 0.17 mole) was then added to the flask over a one hour period, and the reaction was heated to reflux. After three hours at reflux, the reaction mixture was transferred to a separatory funnel, while hot, and washed with a saturated aqueous solution of sodium bicarbonate. The organic layer was separated from the water layer, and washed twice with hot deionized water. The washes were performed at 500°C to facilitate the separation of the two layers. The water and cyclohexane were then evaporated from the organic layer, under vacuum, to yield 145 grams of a pale-yellow, viscous liquid. End-group molecular weight analysis gave a molecular weight of 880 (theoretical molecular weight = 993).

Example 5
Preparation of Poly(nonylphenol glycidyl ether)

To a 500 milliliter round bottom equipped with an overhead stirrer, nitrogen inlet, reflux condenser, additional funnel, and temperature controller was charged 1.9 grams of ethanol (22 mmoles) and 2000 grams of cyclohexane. The solution was brought to 50°C. Once heated, 0.5 milliliters (4 mmoles) of BF_3/Et_2O was added using a 2 milliliter syringe. Once the acid was added, 100.0 grams of nonylphenol glycidyl ether (362 mmoles) was added dropwise so as to

maintain a reactidon temperature of 45°C-55°C. Once the glycidyl ether was added, , the solution is refluxed for 3 hours, then cooled to about 50°C.

Whilile hot (<60°C) the organic was transferred to a separatory funnelel and was washed once with 100 milliliters of 5% sodium bicarbonaate solution. The aqueous layer was drained and the organic was washhed two more times with 100 milliliter portions of deionized water. The aqueous layers were decanted and the organic was dried for at ldeast 1 hour over magnesium sulfate. Once dry the magnesium sulfatate was filtered from the organic which was stripped of solvent using aa rotary evaporator. The final yield of viscous polymer was 100) grams. The GPC molecular weight was Mw = 2600 and the Mn = 17000 based on monodisperse polystyrene standards.

<u>Example 6</u>

<u>Ethoxxylation of Poly(nonylphenol glycidyl ether)</u>

To a a 500 milliliter stainless steel Zipperclave was added 60.0 grams (0.0355 moles based on an approximate molecular weight of 1700 gram/molele) of the resin prepared in Example 5 along with 0.5 grams of potassiuum hydroxide. The vessel was attached to an automated ethoxyylation unit and was heated to 50°C. The vessel was continuously purgged with nitrogen for 15 minutes and was then heated to 100°C vwhere it was again continuously purged with nitrogen for anotther 15 minutes. The vessel was then heated to 140°C and was given a s series of 6 purges by pressuring the vessel up to 80 psi, and then vennting. Once the venting process was complete, the vessel was pressuured to 20 psi with nitrogen.

The e ethylene oxide lines were opened to the motor valves along with the maain feed line on the Zipperclave. The feed was continued and thae vessel pressure was regulated at 55 psi and a temperature of 1440°C. The automation was designed to hold the temperature and 1 the pressure within safe operating limits while

addition of ethylene oxide proceeded through a pair of motor control valves. The feed was allowed to continue until 60.0 grams of ethylene oxide (1.362 moles) was added based on a difference weight of the feed cylinder. After the feed was complete, the reaction was allowed to continue for 1 hour after which the vessel was cooled to 60°C, purged 4 times with nitrogen to 80 psi and was dumped to a container. The final product yield was 115 grams with a theoretical yield of 120 grams. The GPC molecular weight of the product was Mw = 3550 and the MN = 22930 based on monodisperse polystyrene standards.

Example 7

Preparation of Poly(phenyl glycidyl ether)

To a 500 milliliter round bottom equipped with an overhead stirrer, nitrogen inlet, reflux condenser, addition funnel, and temperature controller was charged 47.06 grams of phenol (500 mmoles) and 1000 grams of toluene. The solution was brought to 50°C. Once heated, 1.00 milliliter (8 mmoles) of BF_3/Et_2O was added using a 2 milliliter syringe. Once the acid was added, 68.18 grams of phenyl glycidyl ether (4454 mmoles) was added dropwise so as to maintain a reaction temperature of 45°C-55°C. Once the glycidyl ether was added, the solution is refluxed for 3 hours, then cooled to about 50°C.

While hot (<60°C) the organic was transferred to a separatory funnel and was washed once with 100 milliliters of 5% sodium bicarbonate solution. The aqueous layer was drained and the organic was washed two more times with 100 milliliter portions of deionized water. The aqueous layers were decanted and the organic was dried for at least 1 hour over magnesium sulfate. Once dry the magnesium sulfate was filtered from the organic which was stripped of solvent using a rotary evaporator. The final yield of viscous polymer was 90.3 grams (with 11% unreacted phenol). The GPC molecular weight was Mw = 470 and the Mn = 310 (on average a trimer) based on monodisperse polystyrene standards.

Example 8
Preparation of 1,3-Bis(phenoxy)-2-propanol using the Cascading Polyol Technique

To a 1 liter round bottom flask equipped with an overhead stirrer, nitrogen inlet, reflux condenser, addition funnel, and temperature controller was charged 94.11 grams of phenol (1 mole), 12.86 grams of tetraethylammonium iodide (0.05 moles), 3.00 grams of water (0.17 moles), 42.08 grams of potassium hydroxide (0.75 moles), and 250 grams of toluene. To a 100 milliliter additional funnel was charged 23.13 grams of epichlorohydrin (0.25 moles) and 50 grams of toluene. The solution was brought to 65°C at which time the epichlorohydrin solution was added over a period of 15 minutes while maintaining a reaction temperature of 65°C ± 5°C. The reaction was allowed to proceed for 48 hours.

After 48 hours, the solution was cooled down to room temperature. The toluene solution was washed with two 250 milliliters portions of deionized water. The aqueous layers were drained off, and the toluene was removed along with unreacted phenol using a rotary evaporator. The final yield of product was 64.5 grams which was 106% of theory (residual is phenol). Final product purity was about 95% as shown by GPC.

Example 9
Dimerization of 1,3-Bis(phenoxy)-2-propanol using the Cascading Polyol Technique

To a 250 milliliter round bottom flask equipped with an overhead stirrer, nitrogen inlet, reflux condenser, additional funnel, and temperature controller was charged 20.03 grams of 1,3-bis-

(phenoxy)-2-propanol prepared in Example 8 (82 mmoles), 2.06 grams of tetraethylammonium iodide (8 mmoles), 0.49 grams of water (27 mmoles), 6.51 grams of potassium hydroxide (116 mmoles), and 125 grams of toluene. To a 100 milliliter addition funnel was charged 3.61 grams of epichlorohydrin (39 mmoles) and 25 grams of toluene. The solution was brought to 65°C at which time the epichlorohydrin solution was added over a period of 15 minutes while maintaining a reaction temperature of 65°C ± 5°C. The reaction was allowed to proceed for 48 hours.

After 48 hours, the solution was cooled down to room temperature. The toluene solution was washed with two 250 milliliter portions of deionized water. The aqueous layers were drained off, and the toluene was removed using a rotary evaporator. The final yield of product was 21.6 grams which was 101% of theory. GPC showed two major components of the product. The first was the starting material at about 41% (Mn = 220) and the second was the coupled product at about 59% (Mn = 520).

Example 10
Preparation of 1,3-Bis(hexadecyloxy)-2-propanol using the Cascading Polyol Technique

To a 500 milliliter round bottom flask equipped with an overhead stirrer, nitrogen inlet, reflux condenser, additional funnel, and temperature controller was charged 60.61 grams of hexadecanol (0.25 moles), 6.18 grams of tetraethylammonium iodide (0.024 moles), 1.44 grams of water (0.082 moles), 20.20 grams of potassium hydroxide (0.36 moles), and 125 grams of toluene. To a 100 milliliter addition funnel was charged 11.10 grams of epichlorohydrin (0.12 moles) and 25 grams of toluene. The solution was brought to 65°C at which time the epichlorohydrin solution was added over a period of

15 minutes while maintaining a reaction temperature of 65°C ± 5°C. The reaction was allowed to proceed for 48 hours.

After 48 hours, the solution was cooled down to room temperature. The toluene solution was washed with two 250 milliliter portions of deionized water. The aqueous layers were drained off, and the toluene was removed using a rotary evaporator. The final yield of product was 70.9 grams which is 109% of theory (residual is hexadecanol).

Example 11

Sulfation of 1,3-Bis(nonylphenoxy)-2-propanol-block-(propylene oxide)$_{10}$-block-(ethylene oxide)$_{10}$

To a 250 milliliter round bottom flask equipped with an overhead stirrer, a temperature controller, and a vacuum adapter was added 75.0 grams of the material from Example 13 (49 mmoles). The kettle was then evacuated to <20 mmHg and heated to 100°C to remove any water. After 1 hour, the kettle was cooled to 60°C while under vacuum. When reaching 60°C, vacuum was broken with nitrogen and 5.3 grams of sulfamic acid (54 mmoles) was added. After charging the sulfamic acid, the kettle was heated to 110°C and evacuated to <200 mm Hg. The reaction was allowed to proceed for 3 hours.

At the end of the hold period, the kettle was cooled to 85°C and vacuum was broken with nitrogen. 1.2 grams of diethanolamine (11 mmoles) was slowly added under a blanket of nitrogen. This solution was stirred for 30 minutes. 10 grams of ethanol was added to the kettle and the temperature was regulated to 55°C. This solution was stirred for 30 minutes. The heat was removed from the kettle and 30 grams of water along with 20 grams of ethanol were added while maintaining good agitation. The

solution was stiirred for 15 minutes or until cooled to room temperature (<≤35°C).

Thae pH was checked by dissolving 2 grams of the product solution in 18 ggrams of deionized water. If the pH was below 6.5, 0.2 gram incrementts of diethanolamine was added until the pH is between 6.5 andd 7.5.

Example 12
Preparation of 1,3-Bis(nonylphenoxy)-2-propanol-block-(propylene oxide)$_{10}$

To a 500 milliliter stainless steel Zipperclave was added 100.0 grams (0.202 moles) of 1,3-bis(nonylphenoxy)-2-propanol prepared in Exaample 1 along with 0.7 grams of potassium hydroxide. The vessel was attached to an automated unit and was heated to 50°C. The vessel was continuously purged with nitrogen for 15 minutes and waas then heated to 100°C where it was again continuously puurged with nitrogen for another 15 minutes. The vessel was then heated to 140°C and is given a series of 6 purges by pressuring the vessel up to 80 psi, and then venting. Once the venting process was completed, the vessel was pressured to 20 psi with nitrogen.

Linnes connected to a cylinder which had been precharged withh 117.0 grams of propylene oxide (2.02 moles) were opened to the mnotor valves along with the main feed line on the Zipperclave. The feed was continued and the vessel pressure was regulated at 55 psi and a temperature of 140°C. The automation was designed to holdd the temperature and the pressure within safe operating limits while addition of ethylene oxide proceeded through a pair of motor control valves. The feed was allowed to continue until all of the propylene oxide had been fed. After the feed was complete, the reaction waas allowed to continue for 1 hour after which the vessel

was cooled to 60°C, purged 4 times with nitrogen to 80 psi and was dumped to a conhtainer. The final product yield was 211 grams with a theoretical yield l of 277 grams. The GPC molecular weight of the product was Mw v = 650 and the Mn = 490 based on monodisperse polystyrene stanndards.

Example 13

Preparation of f 1,3-Bis(nonylphenoxy)-2-propanol- block-(propylene oxide)$_{10}$-block-(ethylene oxide)$_{10}$

To aa 500 milliliter stainless steel Zipperclave was added 75.0 grams of thae propoxylate prepared in Example 12 (0.070 moles) along with 0.3 ggrams of potassium hydroxide. The vessel was attached to an auutomated ethoxylation unit and was heated to 50°C. The vessel was ccontinuously purged with nitrogen for 15 minutes and was then heeated to 100°C where it was again continuously purged with nitrrogen for another 15 minutes. The vessel was then heated to 140°C and was given a series of 6 purges by pressuring the vessel up to 80 ppsi, and then venting. Once the venting process was completed, the vvessel was pressured to 20 psi with nitrogen.

Thee ethylene oxide lines were opened to the motor valves along with the mnain feed line on the Zipperclave. The feed was continued and thhe vessel pressure was regulated at 55 psi and a temperature of 1140°C. The automation was designed to hold the temperature andd the pressure within safe operating limits while addition of ethyldene oxide proceeded through a pair of motor control valves. The feedd was allowed to continue until 30.7 grams ethylene oxide (0.696 moldes) was added based on a difference weight of the feed cylinder. After tlthe feed was complete, the reaction is allowed to continue for 1 hoour after which the vessel was cooled to 60°C, purged 4 times with nitrrogen to 80 psi and was dumped to a container. The

final product yield was 99 grams with a theoretical yield of 106 grams.

Example 14
Preparation of Bis(nonylphenoxy) Adduct of 1,4-Butanediol Diglycidyl Ether

To a five neck, two liter round bottom flask equipped with an addition funnel, thermometer, nitrogen dispersant tube, mechanical stirrer, and a decanting head with a water-cooled condenser were added 506.8 grams (2.30 mole) of nonylphenol and 350 milliliters of cyclohexane. The solution was heated to reflux, and 6.5 grams (1.3 weight percent based on nonylphenol) of potassium hydroxide in 15 milliliters of water was slowly added to the round bottom flask. After all the water was recovered in the decanting head (15 milliliters + 2 milliliters formed), 220 grams (1.09 mole) of 1,4-butanediol diglycidyl ether was added dropwise between 60 and 80°C. After the addition was complete, the solution was refluxed for four hours. The contents of the flask were then washed with a five percent aqueous solution of phosphoric acid, and the organic layer was separated from the water layer and washed twice with deionized water. The reaction mixture was then placed in a one liter round bottom flask, and the remaining cyclohexane and unreacted nonylphenol were recovered by distillation, first at atmospheric pressure, then under vacuum at 0.2 mm Hg. The kettle temperature was not allowed to exceed 180°C during the distillation to prevent discoloration of the product. The concentrated solution was then refiltered to give 710 grams of a pale-yellow liquid. Molecular weight by end-group MW analysis was 689.9 (theoretical MW = 643.0). Ir and nmr spectra were consistent with the expected structure of the product.

Example 15
Preparation of 3 Mole Ethoxylate of
1,3-Bis(nonylphenoxy)-2-propanol

To a five hundred milliliter Zipperclave reactor were charged, under nitrogen, 200.1 grams (0.43 mole) of 1,3-bis(nonylphenoxy)-2-propanol prepared in Example 2 and 0.20 grams (0.1 weight percent) of BF_3/Et_2O. The reaction mixture was heated to 80°C, and 55.1 grams (1.25 mole) of ethylene oxide was fed to the reactor over a two hour period. After all the ethylene oxide was fed, the reaction mixture was allowed to cook out for one hour and then dumped hot, under nitrogen, into a jar containing 160 milliliters of a one percent aqueous solution of sodium hydroxide. The organic layer was separated from the water layer and washed twice with deionized water. The washes were performed at 90°C to facilitate the separation of the two layers. The product was then dried by azeotropic removal of the water, using cyclohexane (300 milliliters) as the entrainer. The cyclohexane was stripped off under vacuum to give a pale-yellow liquid with a molecular weight by end-group MW analysis of 601.77 (theoretical MW = 629). Ir and nmr spectra were consistent with the expected structure of the product.

Example 16
Preparation of 8 Mole Ethoxylate of
Bis(nonylphenoxy) Adduct of 1,4-Butanediol
Diglycidyl Ether

To a five hundred milliliter Zipperclave reactor were charged, under nitrogen, 150.2 grams (0.22 mole) of bis(nonylphenoxy) adduct of 1,4-butanediol diglycidyl ether prepared in Example 14 and 0.30 grams (0.2 weight percent) of BF_3/Et_2O. The reaction mixture was heated to 80°C, and 77.5 grams (1.76 mole) of

ethylene oxide ı was fed to the reactor over a two hour period. After all the ethylene oxxide was fed, the reaction mixture was allowed to cook out for one houur and then dumped hot, under nitrogen, into a jar containing 160) milliliters of a one percent aqueous solution of sodium hydroxide. Thae organic layer was separated from the water layer and washed twwice with deionized water. The washes were performed at 90°C to faciliilitate the separation of the two layers. The product was then dried by aazeotropic removal of the water, using cyclohexane (300 milliliters) as tlthe entrainer. The cyclohexane was stripped off under vacuum to givee a pale-yellow liquid with a molecular weight by end-group MW anablysis of 1047 (theoretical MW = 995). Ir and nmr spectra were cconsistent with the expected structure of the product.

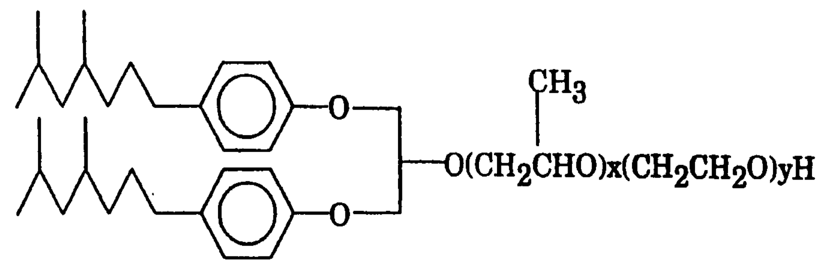
<u>Examples 17 to 21</u>

<u>Preparationn of Propylene Oxide and Ethylene Oxide/Propylene Oxide CCopolymers of 1,3-Bis(nonylphenoxy)-2-propanol</u>

To'o a 500 milliliter stainless steel autoclave was charged an amount of ppotassium hydroxide and starter listed in Table A below. The vesssel was heated to 50° C. The vessel was continuously purged with niitrogen for 15 minutes, and was then heated to 100° C, where it was aagain continuously purged with nitrogen for another 15 minutes. The ı vessel was then heated to 140° C, and was given a series of 6 purgges by pressurizing the vessel up to 80 psi, and then venting. Oncee the venting process was completed, the vessel was pressurized to) 20 psi with nitrogen. The feed lines from an oxide feed cylinder (contaaining a charge of ethylene oxide or propylene oxide as identifed in Tabble A) to the autoclave were opened. The control system fed thee oxide at a rate such that the vessel pressure was regulated at 555 psi and a temperature of 140° C. The reaction was allowed to contitinue for 1 hour past the end of the oxide feed. The vessel was coolbled to 60° C, purged 4 times with nitrogen to 80 psi, and its contents weere dumped into a tared container. The final

theoretical and ε actual product yields and molecular weights determined by ggel permeation chromatography are listed in Table A.

TABLE A



Example	Product Structure x	Product Structure y	Starter Structure x	Starter Structure y	grams Starter	grams KOH	grams PO	grams EO	Theory yield	Actual yield	Mn	Mw	Surface Tension[a]	CMC[b]
17	10	40	10	0	50	0.3	0	82	132	127	2110	2340	43.3	.005
18	10	70	10	0	50	0.3	0	145	193	188	2720	3050	47.1	.005
19	20	0	0	0	50	0.5	117	0	167	162	1270	1530	c	c
20	20	40	20	0	50	0.3	0	54	104	104	2280	2570	42.6	.04
21	20	70	20	0	50	0.3	0	99	149	145	2720	3060	44.2	.03

a - surface tension in dynes/cm at 1 wt.% copolymer in water

b - approximate critical micelle concentration

c - water insoluble

Examples 22-33

Prepparation of Poly(nonylphenyl glycidyl ether)

An ı amount of ethanol listed in Table B below, and 200 grams of cyclohaexane were charged to a 500 milliliter round bottom flask equipped v with an overhead stirrer, nitrogen inlet, reflux condenser, addiition funnel, and temperature controller. The solution was heaated to 50° C after which an amount of boron trifluoride etherrate listed in Table B was added. Subsequently, 100 grams of nonylpphenyl glycidyl ether was added dropwise to the reaction mixturee so as to maintain a reaction temperature of 45-55° C. The solutionn was refluxed at 83° C for an additional three hours after the completetion of feed, and then cooled to 50° C. While hot (<60° C), the organic ı material was transferred to a separatory funnel, and was washed oncce with 100 milliliters of 5% sodium bicarbonate solution. The aaqueous layer was washed two more times with 100 milliliter portionns of deionized water. The aqueous layers were decanted, and tthe organic layer was dried for at least 1 hour over magnesium sulflfate. Once dry, the magnesium sulfate was filtered from the organiclc material, which was stripped of solvent using a rotary evaporattor. The molecular weights of the polymer based on gel permeation (chromatography are listed in Table B.

Table B

Example	mL BF_3/Et_2O	Grams Ethanol	Mn	Mw
22	00.5	1.9	1700	2600
23	11.25	10.0	410	450
24	00.5	5.5	470	560
25	11.25	5.5	870	1150
26	11.25	1.0	1580	2530
27	22.0	5.5	900	1190
28	22.0	1.0	1470	2310
29	22.0	10.0	440	500

Table B
(Continued)

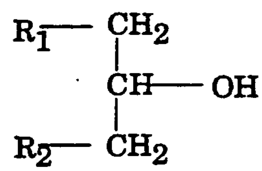
Example	mL BF_3/Et_2O	Grams Ethanol	Mn	Mw
30	00.5	10.0	580	730
31	00.5	1.0	1750	2790
32	00.5	1.0	1740	2640
33	11.6	3.32	1170	1570

Examples 34-36

Preparation of Unsymmetric Biphobes

To a 500 milliter round bottom flask equipped with an overhead stirrer, nitrogen inlet, reflux condenser, addition funnel, and temperature controller was charged an amount of starting alcohol listed in Table C below. The material was heated to 170° C under nitrogen sparge, after which an amount of potassium hydroxide listed in Table C was added. An amount of epoxide listed in Table C was fed to the reaction flask using an FMI feed pump at a rate such that addition of the epoxide was completed in 6 hours. Gel permeation chromatography showed that the purity of the biphobic product was greater than 90%.

Table C



Ex.	Alcohol	Gms Alch.	Gms KOH	Epoxide	Grams Epoxide	R1	R2
34	nonyl-phenol	100	2	1,2 epoxy-hexadecane	108.6	nonyl-phenoxy	tridecyl
35	dodecyl-phenol	100	2	1,2 epoxy-hexadecane	91.1	dodecyl-phenoxy	tridecyl
36	dodecyl-phenol	50	1	nonylphenyl glycidyl ether	52.7	dodecyl-phenoxy	nonyl-phenoxy

Example 37

Preparation of Poly(1,2-epoxyhexadecane)

The process described in Examples 34-36 was used with 50 grams of 1-hexadecanol, 1 gram of potassium hydroxide, and 49.4 grams of 1,2 epoxyhexadecane. The product multiphobe had a composition of 10% hexadecanol, 55.5% biphobe (i.e., 1-hexadecoxy-2-hexadecanol), 27.7% triphobe, and 6.5% quadphobe, as determined by gel permeation chromatography.

Example 38

Preparation of an Unsaturated Poly(nonylphenyl glycidyl ether)

To a 500 milliliter round bottom flask equipped with an overhead stirrer, nitrogen inlet, reflux condenser, addition funnel, and temperature controller was charged 10 grams of allyl alcohol, 40

grams of toluenne, 0.5 grams of potassium hydroxide, and 2 grams of deionized wateer. The reaction mixture was refluxed to dryness, and cooled to 60° C.. Once cool, 47.6 grams of nonylphenyl glycidyl ether was fed to the r reaction vessel using a FMI pump over 35 minutes. The reaction miixture was heated to 112° C, and refluxed for 3 hours. The solvent waas removed from the reaction mixture by vacuum stripping. The product was cooled and recovered. The product composition waas 15% allyl alcohol, 43% biphobe (e.g., 1-(2-propene-1-oxy)-3-nonylphenoxy-2-propanol) and 42% triphobe, as determined by gel permeationn chromatography.

Example 39

SSolventless Macromonomer Preparation

Too a 3 liter round bottom flask equipped with an overhead stirreer, nitrogen inlet and sparging tube, water cooled reflux condenseer, monomer addition tube, FMI pump and feed tank, and heating maantel and temperature controller, 2000 grams of previously meltlted surfactant S-2 were charged. The materials were heated to 85° CC under nitrogen sparge and mixing, and held at temperature foor 1 hour to drive off residual water. Then 0.05 grams of 4-methoxyphhenol were added, and the mixture was sparged with air for 15 minututes to activate the inhibitor. 2.4 grams of dibutyl tin dilaurate were added, and after 15 minutes of mixing, 201.25 grams of TMI were fedd over 45 minutes. The mixture was held at 85° C for another 4 hourss. Then 243 grams of water was pumped into the reaction mixturre over a 25 minute period to wash the feed lines of isocyanate, andd to dilute the product macromonomer to 90% solids. The product maacromonomer was cooled and collected in a 1 gallon jug.

Example 40

Preparation of Macromonomer Compound

Into a 1 liter round bottom reaction flask equipped with a heating mantle, dean stark trap, condenser, thermometer, nitrogen bubbler, nitrogen purge line and stirrer was charged 300 grams of toluene and 63 grams of a surfactant identified as S-1 in Table D below. With nitrogen purge, the resulting solution was heated to reflux at approximately 110°C and azeotroped to remove trace water to dryness. The solution was subsequently cooled to 90°C, and 1.5 grams of bismuth hex chem 28% bismuth octoate catalyst (Mooney Chemical, Inc., Cleveland, Ohio) was charged and allowed to mix well, after which a stoichiometric amount of 95% m-TMI aliphatic isocyanate (American Cyanamid, Stamford, Connecticut) was charged. After the reaction proceeded at 90°C for 1.3 hours, the resulting product was cooled to 70°C and 0.03 grams of 2,6-di-tert-4-methyl phenol (BHT) preservative was added. The mixture was poured into a stainless steel pan with large surface area to facilitate drying. The final product was a waxy material, and is designated herein as macromonomer M-1.

Table D

$$
\begin{array}{l}
R_1\text{-O-}CH_2 \\
\quad | \\
\quad CH\text{-}(OCH_2CH_2)_xOCH_2CH_2OH \\
\quad | \\
\quad R_2
\end{array}
$$

R_2 = hydrogen or a R_3-O-CH_2- residue.

Surfactant	R_1	R_2/R_3	Moles of Ethoxylation
S-1	Noonylphenol	Hydrogen (R_2)	40
S-2	Noonylphenol	Nonylphenol (R_3)	40
S-3	Noonylphenol	Nonylphenol (R_3)	20
S-4	Noonylphenol	Octylphenol (R_3)	20
S-5	Noonylphenol	Octylphenol (R_3)	40
S-6	Noonylphenol	Nonylphenol (R_3)	80
S-7	Noonylphenol	Nonylphenol (R_3)	120
S-8	Noonylphenol	Nonylphenol (R_3)	6
S-9	Noonylphenol	Nonylphenol (R_3)	12

Examples 41-61

Prreparation of Macromonomer Compounds

In a manner similar to that described in Example 40, other macromoonomers were prepared using stoichiometric amounts of the surfactannts and unsaturated compounds identified in Table E below.

Table E

Example No.	Suurfactant	Unsaturated Compound	Macromonomer Designation
41	SS-2	m-TMI	M-2
42	SS-3	m-TMI	M-3
43	SS-4	m-TMI	M-4
44	SS-5	m-TMI	M-5
45	SS-6	m-TMI	M-6
46	SS-7	m-TMI	M-7
47	SS-2	Isocyanato Ethyl Methacrylate	M-8

Table E
(Continued)

Example No.	Surrfactant	Unsaturated Compound	Macromonomer Designation
48	S-5	Isocyanato Ethyl Methacrylate	M-9
49	S-1	Methacrylic Anhydride	M-10
50	S-2	Methacrylic Anhydride	M-11
51	S-5	Methacrylic Anhydride	M-12
52	S-6	Methacrylic Anhydride	M-13
53	S-2	Acrylic Anhydride	M-14
54	S-5	Acrylic Anhydride	M-15
55	S-6	Acrylic Anhydride	M-16
56	S-2	Crotonic Anhydride	M-17
57	S-5	Maleic Anhydride	M-18
58	S-2	Methacryloyl Isocyanate	M-19
59	S-6	Methacryloyl Isocyanate	M-20
60	S-8	m-TMI	M-21
61	S-9	m-TMI	M-22

Example 62
PPreparation of Alkali Soluble Thickener

A mmonomer mixture (300 grams) was prepared by charging ethyl aacrylate (Aldrich), methacrylic acid (Aldrich), macromonomer M-1, 13 grams of a 75% solution of Aerosol OT surfactant (Ameerican Cyanamid, Stamford, Connecticut), and 3 grams of distilleed deionized water to a bottle, and dispersing the contents with vigigorous shaking. The ethyl acrylate, methacrylic acid and macromonoomer M-1 were added in amounts identified in Table F below. A catallyst feed mixture comprised of 0.53 grams of sodium persulfate (Aldririch) and 52.47 grams of water was prepared in

another containner. To a 2 liter resin flask that had been immersed in a thermostated l water bath and equipped with a 4-bladed stainless steel mechanicaal stirrer, Claisen connecting tube, water condenser, nitrogen spargge and bubble trap, thermometer and monomer and catalyst additioon inlets, 1.20 grams of the sodium salt of vinyl sulfonic acid and 658.5 grams of water were charged. The monomer mixture was charged to a 1-liter graduated monomer feed cylinder, and the catalyst solutionn was charged to a 125 milliliter graduated catalyst feed cylinder. Under nitrogen purge, the reactor was heated to 70°C, whereupon 33 milliliters of the monomer mixture and 3 milliliters of the catalyst feeed mixture were charged to the reaction vessel. The reaction vessel was subsequently heated to 80°C. After allowing the monomers to reeact for 20 minutes to form a seed product, the monomer and ccatalyst feed mixtures were conveyed to the reaction vessel by FMI ppumps via 1/8" teflon tubing at a rate of 1.94 and 0.27 milliliters/minute, respectively, under continuous stirring at a reaction temperrature held between 76-82°C. The reaction was allowed to procceed for another hour, after which the product was cooled and filterred with a 200 mesh nylon cloth. The coagulum was collected from tthe reaction vessel and filter cloth. Thickening ability of the resulting product was monitored by Brookfield viscosity at 6 rpm by dilutingg the latex to 0.25%, 0.50% and 0.75% solids, and subsequently neeutralizing the product to pH=9.0 with a 95% solution of 2-amino-2-methyl-1- propanol (AMP-95, Angus Chemical Company). Thae results are given in Table F.

Examples 63-174

Preparation of Alkali Soluble Thickeners

In a manner similar to that described in Example 62, other alkali solluble thickeners were prepared using the monomers identified in Tabbles F-Q below in the amounts identified in Tables F-Q. Tables F anod G illustrate the influence of m-TMI-containing

macromonomer (concentration and ethoxylation on thickening efficiency. Table.e H illustrates the influence of 2-SEM on thickening efficiency. Tablde I illustrates the influence of mixing m-TMI-containing macrromonomers of various ethoxylations on thickening efficiency. Tablele J illustrates the influence of unsaturation type of urethane-containining macromonomers on thickening efficiency. Table K illustratites the influence of methacryloyl isocyanate incorporated intdo the macromonomer. Table L illustrates the influence of macicromonomer ester structure and ethoxylation on thickening efficiciency. Table M illustrates the influence of acid type and concentratio.on on thickening efficiency. Table N illustrates the influence of polyymer glass transition temperature and water solubility on thicickening efficiency. Table O illustrates the influence of acrylamide inacorporated into the macromonomer. Table P illustrates the iiinfluence of cross-linkable monomer concentration on thickening efficiciency. Table Q illustrates the influence of mercaptan on thickening effficiency. As used in Tables F-Q below, the following abbreviations haave the indicated meanings: MM = Macromonomer; EA = Ethyl Acryylate; MAA = Methacrylic Acid; AA = Acrylic Acid; MA = Methyl Acxcrylate; t-BA = t-Butyl Acrylate; n-BA = n-Butyl Acrylate; MMA == Methyl Methacrylate; 2-EHP = 2-Ethylhexyl Propionate Merc:captan; 2-SEM = 2-sulfoethyl methacrylate; and 2-HEA = 2-Hydroxxy Ethyl Acrylate.

TABLE F

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.50%	0.75%	Thickener Designation
62	M-1	10	50	40	90	380	1,000	P-1
63	M-2	5	55	40	270	11,400	103,600	P-2
64	M-2	10	50	40	120	3,100	60,000	P-3
65	M-2	10	50	40	105	10,400	130,000	P-3a
66	M-2	20	40	40	25	2,150	50,500	P-4
67	M-2	30	30	40	10	790	20,000	P-5
68	M-3	5	55	40	390	2,260	17,900	P-6
69	M-3	6.5	53.5	40	142	1,200	18,500	P-7
70	M-3	10	50	40	220	3,050	40,000	P-8
71	M-3	20	40	40	75	2,350	27,500	P-9
72	M-4	10	50	40	242	4,400	39,000	P-10
73	M-5	10	50	40	45	7,400	84,000	P-11
74	M-5	20	40	40	34	4,450	59,000	P-12
75	M-6	5	55	40	460	25,500	88,000	P-13
76	M-6	10	50	40	105	39,000	150,000	P-14
77	M-6	15	45	40	195	43,000	140,000	P-15
78	M-6	20	40	40	125	52,500	187,000	P-16
79	M-6	30	30	40	315	56,500	162,000	P-17
80	M-7	5	55	40	230	7,800	15,800	P-18
81	M-7	10	50	40	900	17,400	35,000	P-19

TABLE G

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.5%	.75%	1%
82	M-21	10	50	40	120	117	110	125
83	M-22	10	50	40	122	190	335	950

TABLE H

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	% 2-SEM	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.5%	.75%
84	M-6	10	50	35	5	23	4,340	32,000
85	M-6	10	50	30	10	<10	510	6,400

TABLE I

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.5%	.75%	Thickener Designation
86	M-3:M-6 1:1	10	50	40	225	24,000	85,000	P-20
87	M-2:M-6 1:1	10	50	40	135	21,200	134,000	P-21

TABLE J

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.5%	.75%	Thickener Designation
88	M-8	5	55	40	250	14,800	124,000	P-22
89	M-8	10	50	40	93	11,200	125,400	P-23
90	M-8	20	40	40	45	6,140	84,500	P-24
91	M-9	5	55	40	275	6,200	57,000	P-25
92	M-9	10	50	40	250	10,100	80,000	P-26
93	M-9	20	40	40	90	7,800	90,000	P-27
94	M-9	30	30	40	45	5,200	69,000	P-28

TABLE K

Example	Macromonomer	Thickener Composition Weight %MM	%EA	%MAA	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.5%	.75%
95	M-19	5	55	40	167	4,050	28,000
96	M-19	10	50	40	652	22,000	88,500
97	M-19	20	40	40	1,710	34,200	128,000
98	M-19	30	30	40	2,125	61,300	155,000
99	M-20	5	55	40	344	10,960	30,300
100	M-20	10	50	40	1,115	29,000	68,500
101	M-20	20	40	40	2,175	45,500	129,000
102	M-20	30	30	40	2,400	61,000	150,000

Table L

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.50%	0.75%	Thickener Designation
103	M-10	10	50	40	130	285	410	P-29
104	M-11	10	50	40	190	19,500	152,000	P-30
105	M-11	20	40	40	120	13,500	146,000	P-31
106	M-11	30	30	40	96	8,000	73,000	P-32
107	M-12	5	55	40	260	5,400	51,000	P-33
108	M-12	10	50	40	175	9,200	71,000	P-34
109	M-12	20	40	40	100	7,400	77,000	P-35
110	M-12	30	30	40	62	4,500	63,000	P-36
111	M-13	5	55	40	320	25,600	79,000	P-37
112	M-13	10	50	40	97	28,000	125,000	P-38
113	M-13	20	40	40	300	58,200	171,000	P-39
114	M-13	30	30	40	730	63,000	163,000	P-40
115	M-14	10	50	40	410	22,700	130,000	P-41
116	M-14	20	40	40	1225	44,500	168,000	P-42
117	M-14	30	30	40	1010	42,500	180,000	P-43
118	M-15	5	55	40	84	1,680	29,000	P-44
119	M-15	10	50	40	350	12,000	83,000	P-45
120	M-15	20	40	40	220	24,500	122,000	P-46
121	M-15	30	30	40	1050	33,000	133,000	P-47
122	M-16	5	55	40	450	17,720	45,300	P-48
123	M-16	10	50	40	1,345	27,000	98,000	P-49
124	M-16	20	40	40	3,450	65,800	158,000	P-50
125	M-16	30	30	40	11,600	81,000	157,000	P-51
126	M-17	10	50	40	410	12,000	60,000	P-52
127	M-17	20	40	40	255	10,600	46,300	P-53
128	M-17	30	30	40	38	2,525	13,500	P-54
129	M-18	5	55	40	100	810	3,500	P-55
130	M-18	10	50	40	110	1,420	5,940	P-56
131	M-18	20	40	40	30	870	2,425	P-57

Table M

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	%AA	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.50%	0.75%	Thickener Designation
132	M-2	10	60	30	0	1520	12,200	102,000	P-58
133	M-2	10	70	20	0	45	3,800	50,000	P-59
134	M-2	10	80	10	0	<10	<10	<10	P-60
135	M-2	10	60	0	30	<10	95	6,800	P-61
136	M-6	20	60	20	0	15	13,500	43,500	P-62
137	M-6	5	65	30	0	210	13,000	56,500	P-63
138	M-6	10	60	30	0	77	24,000	88,000	P-64
139	M-6	20	50	30	0	17	7,600	79,000	P-65
140	M-6	5	45	50	0	130	7,060	28,000	P-66
141	M-6	10	40	50	0	86	16,700	52,500	P-67
142	M-6	20	30	50	0	130	28,000	122,000	P-68
143	M-11	10	70	0	20	<10	213	7300	P-69
144	M-17	10	50	20	20	710	16,500	66,000	P-70

Table N

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	%Other	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.50%	0.75%	Thickener Designation
145	M-2	10	40	40	10 MMA	90	5,760	82,000	P-71
146	M-2	10	30	40	20 MMA	15	1,125	55,000	P-72
147	M-2	10	20	40	30 MMA	10	207	6,000	P-73
148	M-2	10	0	40	50 MMA	<10	<10	<10	P-74
149	M-2	10	30	40	20 styrene	20	310	1,330	P-75
150	M-2	10	40	40	10 styrene	95	7,540	75,500	P-76
151	M-2	10	40	40	10 n-BA	220	13,800	118,000	P-77
152	M-2	10	30	40	20 n-BA	185	7,400	66,500	P-78
153	M-2	10	40	40	10 t-BA	130	10,100	100,000	P-79
154	M-2	10	30	40	20 t-BA	125	7,200	77,500	P-80
155	M-2	10	40	40	10 MA	100	6,900	121,000	P-81
156	M-2	10	30	40	20 MA	73	5,000	90,000	P-82
157	M-6	20	30	40	10 MMA	33	15,400	150,000	P-83

Table Q

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	%Acryl-amide*	Broofield Viscosity (CPS) @ pH=9.0 0.25%	0.5%	.75%
158	none	0	55	35	10	102	137	162
159	M-6	10	45	35	10	112	32,700	124,000
160	M-6	10	50	35	5	71	22,500	110,000
161	M-6	10	55	35	0	115	22,300	104,000

*The amount of acrylamide influences the pH of solubilization for the polymer. The pH of solubility for the polymer is as follows: Example 159 = 5.0; Example 160 = 5.8; and Example 161 = 6.2. The pH of solubility is that pH where the aqueous sample goes from being a low viscosity and turbid latex to a viscous clear solution.

Table P

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	%2-HEA	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.50%	0.75%	Thickener Designation
162	M-2	10	47.7	40	2.3	97	9,060	127,000	P-84
163	M-2	10	57.7	30	2.3	62	6,300	76,000	P-85
164	M-2	20	37.5	40	2.5	27	6,200	116,600	P-86
165	M-2	20	35	40	5	<10	260	18,600	P-87
166	M-2	20	32.5	40	7.5	20	720	40,000	P-88
167	M-2	20	30	40	10	10	520	29,500	P-89

Table Q

Example	Macromonomer	Thickener Composition by Weight %MM	%EA	%MAA	%2-EHP*	Brookfield Viscosity (CPS) @ pH=9.0 0.25%	0.50%	0.75%	Thickener Designation
168	M-2	10	40	50	.05	165	22,800	142,000	P-90
169	M-2	10	50	40	0.2	18	2,060	66,500	P-91
170	M-2	10	50	40	0.3	<10	115	9,700	P-92
171	M-2	10	50	40	0.5	<10	12	355	P-93
172	M-2	10	50	40	1	<10	<10	<10	P-94
173	M-6	10	50	40	.05	230	23,700	90,700	P-95
174	M-6	10	50	40	.2	30	5,170	33,000	P-96

*% charged to reactor based on monomer.

Examples 175-230

Co-Thickening wwith Surfactants

Thee addition of certain surfactants to an associative polymer solutionn produces a co-thickening effect. The results in Table L below shhow the co-thickening effect produced by the addition with thorough mnixing of certain surfactants identified in Table R below in the amaounts identified in Table L to a 0.5% alkaline solution of an alkali solubble thickener identified in Table S as measured with a Brookfield Viscicometer at 6 rpm at pH = 9.0.

Table R

$$
\begin{array}{l}
R_1\text{-O-}CH_2 \\
\quad\quad | \\
\quad\quad CH\text{-}(OCH_2CH_2)_xOCH_2CH_2OH \\
\quad\quad | \\
\quad\quad R_2
\end{array}
$$

R_2 = hydrogen or a R_3-O-CH_2- residue.

Surfactant	R_1	R_2/R_3	Moles of Ethoxylation
S-8	Nonnylphenol	Nonylphenol (R_3)	20
S-9	Nonnylphenol	Nonylphenol (R_3)	40
S-10	Nonnylphenol	Nonylphenol (R_3)	80
S-11	Nonnylphenol	Hydrogen (R_2)	25
S-12	Nonnylphenol	Hydrogen (R_2)	40
S-13	Nonnylphenol	Octylphenol (R_3)	20
S-14	Nonnylphenol	Octylphenol (R_3)	40
S-15*	Nonnylphenol	Nonylphenol (R_3)	40
S-16	Octytylphenol	Hydrogen (R_2)	25

* Sulfated derivative.

Table S

Example	Surfactant	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH=9.0
175	S-8	0.0	P-3	3100
	S-8	0.2	P-3	32700
	S-8	0.4	P-3	45700
	S-8	0.8	P-3	63300
	S-8	1.0	P-3	65500
	S-8	2.0	P-3	>100000
176	S-9	0.2	P-3	24200
	S-9	0.4	P-3	18700
	S-9	0.8	P-3	6600
	S-9	1.0	P-3	4060
		2.0	P-3	1225
177	S-10	0.2	P-3	20600
	S-10	0.4	P-3	17300
	S-10	0.8	P-3	8500
	S-10	1.0	P-3	6300
	S-10	2.0	P-3	1850
178	S-11	0.2	P-3	12000
	S-11	0.4	P-3	3160
	S-11	0.8	P-3	700
	S-11	1.0	P-3	485
	S-11	2.0	P-3	480
179	S-12	0.2	P-3	9200
	S-12	0.4	P-3	4500
	S-12	0.8	P-3	1000
	S-12	1.0	P-3	875
	S-12	2.0	P-3	565
180	S-13	0.2	P-3	34300
	S-13	0.4	P-3	26700
	S-13	0.8	P-3	11500
	S-13	1.0	P-3	8600
	S-13	2.0	P-3	2450

Table S
(Continued)

Example	Surfactant	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH=9.0
181	S-14	0.2	P-3	22200
	S-14	0.4	P-3	17200
	S-14	0.8	P-3	6900
	S-14	1.0	P-3	4500
	S-14	2.0	P-3	1500
182	S-15	0.2	P-3	10500
	S-15	0.4	P-3	4940
	S-15	0.8	P-3	2160
	S-15	1.0	P-3	1450
	S-15	2.0	P-3	355
183	S-16	0.2	P-3	14300
	S-16	0.4	P-3	4080
	S-16	0.8	P-3	1075
	S-16	1.0	P-3	735
	S-16	2.0	P-3	485
184	S-8	0.0	P-2	11400
	S-8	0.2	P-2	23500
	S-8	0.4	P-2	34000
	S-8	0.8	P-2	64000
	S-8	1.0	P-2	71000
	S-8	2.0	P-2	93000
185	S-9	0.2	P-2	11000
	S-9	0.4	P-2	4000
	S-9	0.8	P-2	2000
	S-9	1.0	P-2	1400
	S-9	2.0	P-2	850
186	S-10	0.2	P-2	10500
	S-10	0.4	P-2	5000
	S-10	0.8	P-2	2000
	S-10	1.0	P-2	1600
	S-10	2.0	P-2	950

Table S
(Continued)

Example	Surfactant	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH=9.0
187	S-S-11	0.2	P-2	2700
	S-S-11	0.4	P-2	1000
	S-S-11	0.8	P-2	800
	S-S-11	1.0	P-2	660
	S-S-11	2.0	P-2	620
188	S-S-12	0.2	P-2	2800
	S-S-12	0.4	P-2	1000
	S-S-12	0.8	P-2	850
	S-S-12	1.0	P-2	660
	S-S-12	2.0	P-2	650
189	S-S-8	0.0	P-4	2150
	S-S-8	0.2	P-4	19000
	S-S-8	0.4	P-4	31000
	S-S-8	0.8	P-4	55000
	S-S-8	1.0	P-4	61000
	S-S-8	2.0	P-4	85000
190	S-S-9	0.2	P-4	19500
	S-S-9	0.4	P-4	21500
	S-S-9	0.8	P-4	11500
	S-S-9	1.0	P-4	7400
	S-S-9	2.0	P-4	2250
191	S-S-10	0.2	P-4	12600
	S-S-10	0.4	P-4	17400
	S-S-10	0.8	P-4	12600
	S-S-10	1.0	P-4	6600
	S-S-10	2.0	P-4	2600
192	S-S-11	0.2	P-4	17400
	S-S-11	0.4	P-4	7800
	S-S-11	0.8	P-4	1650
	S-S-11	1.0	P-4	860
	S-S-11	2.0	P-4	560

Table S
(Continued)

Example	Surfactanunt	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH=9.0
193	S-12	0.2	P-4	14600
	S-12	0.4	P-4	7800
	S-12	0.8	P-4	1500
	S-12	1.0	P-4	960
	S-12	2.0	P-4	450
194	S-8	0.0	P-5	790
	S-8	0.2	P-5	4600
	S-8	0.4	P-5	19600
	S-8	0.8	P-5	42000
	S-8	1.0	P-5	50000
	S-8	2.0	P-5	90000
195	S-9	0.2	P-5	5800
	S-9	0.4	P-5	13200
	S-9	0.8	P-5	9200
	S-9	1.0	P-5	5200
	S-9	2.0	P-5	1600
196	S-10	0.2	P-5	4050
	S-10	0.4	P-5	10400
	S-10	0.8	P-5	9400
	S-10	1.0	P-5	5000
	S-10	2.0	P-5	1600
197	S-11	0.2	P-5	10600
	S-11	0.4	P-5	4200
	S-11	0.8	P-5	1400
	S-11	1.0	P-5	970
	S-11	2.0	P-5	410
198	S-12	0.2	P-5	6000
	S-12	0.4	P-5	4200
	S-12	0.8	P-5	1150
	S-12	1.0	P-5	600
	S-12	2.0	P-5	340

Table S
(Continued)

Example	Surfactant	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH=9.0
199	S-8	0	P-7	1200
	S-8	0.2	P-7	9000
	S-8	0.4	P-7	21000
	S-8	0.8	P-7	37000
	S-8	1.0	P-7	49000
	S-8	2.0	P-7	78000
200	S-9	0.2	P-7	1600
	S-9	0.4	P-7	1350
	S-9	0.8	P-7	900
	S-9	1.0	P-7	762
	S-9	2.0	P-7	565
201	S-10	0.2	P-7	1100
	S-10	0.4	P-7	1150
	S-10	0.8	P-7	900
	S-10	1.0	P-7	823
	S-10	2.0	P-7	650
202	S-11	0.2	P-7	1175
	S-11	0.4	P-7	685
	S-11	0.8	P-7	503
	S-11	1.0	P-7	495
	S-11	2.0	P-7	502
203	S-12	0.2	P-7	950
	S-12	0.4	P-7	675
	S-12	0.8	P-7	525
	S-12	1.0	P-7	500
	S-12	2.0	P-7	480
204	S-8	0.0	P-13	25500
	S-8	0.2	P-13	31500
	S-8	0.4	P-13	46500
	S-8	0.8	P-13	60000
	S-8	1.0	P-13	60000
	S-8	2.0	P-13	62500

Table S
(Continued)

Example	Surfactantnt	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH=9.0
205	S-9	0.2	P-13	8640
	S-9	0.4	P-13	2940
	S-9	0.8	P-13	1200
	S-9	1.0	P-13	1000
	S-9	2.0	P-13	750
206	S-10)	0.2	P-13	10100
	S-10)	0.4	P-13	4200
	S-10)	0.8	P-13	1450
	S-10)	1.0	P-13	1300
	S-10)	2.0	P-13	900
207	S-12 :	0.2	P-13	2540
	S-12 :	0.4	P-13	1125
	S-12 :	0.8	P-13	750
	S-12 :	1.0	P-13	670
	S-12 :	2.0	P-13	610
208	S-8	0.0	P-14	39000
	S-8	0.2	P-14	61000
	S-8	0.4	P-14	73500
	S-8	0.8	P-14	87000
	S-8	1.0	P-14	93500
	S-8	2.0	P-14	122000
209	S-9	0.2	P-14	41000
	S-9	0.4	P-14	13700
	S-9	0.8	P-14	6200
	S-9	1.0	P-14	3500
	S-9	2.0	P-14	1200
210	S-10)	0.2	P-14	38200
	S-10)	0.4	P-14	20500
	S-10)	0.8	P-14	7300
	S-10)	1.0	P-14	5400
	S-10)	2.0	P-14	1950

Table S
(Continued)

Example	Surfactanunt	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH=9.0
211	S-12 2	0.2	P-14	13000
	S-12 2	0.4	P-14	4300
	S-12 2	0.8	P-14	975
	S-12 2	1.0	P-14	950
	S-12 2	2.0	P-14	660
212	S-8	0.0	P-16	52500
	S-8	0.2	P-16	95000
	S-8	0.4	P-16	92000
	S-8	0.8	P-16	122000
	S-8	1.0	P-16	125000
	S-8	2.0	P-16	138000
213	PS-9 9	0.2	P-16	73500
	PS-9 9	0.4	P-16	53000
	PS-9 9	0.8	P-16	25000
	PS-9 9	1.0	P-16	21000
	PS-9 9	2.0	P-16	5400
214	S-10 0	0.2	P-16	52800
	S-10 0	0.4	P-16	34500
	S-10 0	0.8	P-16	5400
	S-10 0	1.0	P-16	2925
	S-10 0	2.0	P-16	775
215	S-13 3	0.2	P-16	45800
	S-13 3	0.4	P-16	54000
	S-13 3	0.8	P-16	50800
	S-13 3	1.0	P-16	54500
	S-13 3	2.0	P-16	63000
216	S-14 4	0.2	P-16	22700
	S-14 4	0.4	P-16	2480
	S-14 4	0.8	P-16	710
	S-14 4	1.0	P-16	532
	S-14 4	2.0	P-16	415

Table S
(Continued)

Example	Surfactantnt	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH=9.0
217	S-8	0.0	P-29	285
	S-8	0.2	P-29	285
	S-8	0.4	P-29	360
	S-8	0.8	P-29	477
	S-8	1.0	P-29	505
	S-8	2.0	P-29	837
218	S-9	0.2	P-29	282
	S-9	0.4	P-29	285
	S-9	0.8	P-29	284
	S-9	1.0	P-29	298
	S-9	2.0	P-29	322
219	S-10	0.2	P-29	272
	S-10	0.4	P-29	278
	S-10	0.8	P-29	285
	S-10	1.0	P-29	297
	S-10	2.0	P-29	315
220	S-12	0.2	P-29	267
	S-12	0.4	P-29	279
	S-12	0.8	P-29	298
	S-12	1.0	P-29	311
	S-12	2.0	P-29	320
221	S-8	0.0	P-30	19500
	S-8	0.2	P-30	79000
	S-8	0.4	P-30	71200
	S-8	0.8	P-30	81000
	S-8	1.0	P-30	89500
	S-8	2.0	P-30	175000
222	S-9	0.2	P-30	52000
	S-9	0.4	P-30	35500
	S-9	0.8	P-30	16500
	S-9	1.0	P-30	15600
	S-9	2.0	P-30	5620

Table S
(Continued)

Example	Surfactant	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH=9.0
223	S-10	0.2	P-30	47200
	S-10	0.4	P-30	26300
	S-10	0.8	P-30	20300
	S-10	1.0	P-30	13400
	S-10	2.0	P-30	4700
224	S-12	0.2	P-30	23000
	S-12	0.4	P-30	6840
	S-12	0.8	P-30	3125
	S-12	1.0	P-30	1750
	S-12	2.0	P-30	1225
225	S-8	0.0	P-46	24500
	S-8	0.2	P-46	79000
	S-8	0.4	P-46	75000
	S-8	0.8	P-46	86000
	S-8	1.0	P-46	95000
	S-8	2.0	P-46	150000
226	S-9	0.2	P-46	40500
	S-9	0.4	P-46	31000
	S-9	0.8	P-46	15300
	S-9	1.0	P-46	9400
	S-9	2.0	P-46	2300
227	S-11	0.2	P-46	20000
	S-11	0.4	P-46	7300
	S-11	0.8	P-46	1350
	S-11	1.0	P-46	900
	S-11	2.0	P-46	380
228	S-13	0.2	P-46	63500
	S-13	0.4	P-46	42000
	S-13	0.8	P-46	23000
	S-13	1.0	P-46	16000
	S-13	2.0	P-46	4850

Table S
(Continued)

Example	Surfactantnt	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH=9.0
229	S-14	0.2	P-46	36000
	S-14	0.4	P-46	25000
	S-14	0.8	P-46	11000
	S-14	1.0	P-46	9300
	S-14	2.0	P-46	1900
230	S-16	0.2	P-46	19000
	S-16	0.4	P-46	9300
	S-16	0.8	P-46	1250
	S-16	1.0	P-46	750
	S-16	2.0	P-46	290

Examples 231-275

Co-Thickening wwith Surfactants

The degree of ethoxylation of a surfactant added to an associative polymmer solution influences the co-thickening effect. The results in Table U below show the co-thickening effect produced by the addition withh thorough mixing of certain surfactants identified in Table T below in the amounts identified in Table U to a 0.3% (Examples 172-1889), 0.5% (Examples 190-215) or 0.75% (Example 216) alkaline solution of an alkali soluble thickener identified in Table U as measured withh a Brookfield Viscometer at 6 rpm at pH = 9.0.

$$\begin{array}{l} R_1\text{-O-}CH_2 \\ \qquad\quad | \\ \qquad\quad CH\text{-}(OCH_2CH_2)_xOCH_2CH_2OH \\ \qquad\quad | \\ \qquad\quad R_2 \end{array}$$

R_2 = hydrogen orr a R_3-O-CH_2- residue.

Table T

Surfactant	RR$_1$	R2/R$_3$	Moles of Ethoxylation
S-17	Nonnylphenol	Hydrogen (R$_2$)	4
S-18	Nonnylphenol	Hydrogen (R$_2$)	6
S-19	Nonnylphenol	Hydrogen (R$_2$)	7
S-20	Nonnylphenol	Hydrogen (R$_2$)	8
S-21	Nonnylphenol	Hydrogen (R$_2$)	9
S-22	Nonnylphenol	Hydrogen (R$_2$)	10
S-23	Nonnylphenol	Hydrogen (R$_2$)	15
S-24	Nonnylphenol	Hydrogen (R$_2$)	25
S-25	Nonnylphenol	Hydrogen (R$_2$)	40
S-26	Octtylphenol	Hydrogen (R$_2$)	1
S-27	Octtylphenol	Hydrogen (R$_2$)	3
S-28	Octtylphenol	Hydrogen (R$_2$)	5
S-29	Octtylphenol	Hydrogen (R$_2$)	7
S-30	Octtylphenol	Hydrogen (R$_2$)	9
S-31	Octtylphenol	Hydrogen (R$_2$)	12
S-32	Octtylphenol	Hydrogen (R$_2$)	16
S-33	C111-C15 Seccondary Alccohol	Hydrogen (R$_2$)	5
S-34	C111-C15 Seccondary Aldcohol	Hydrogen (R$_2$)	9

Table U

Example	Surfactant	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH = 9.0
231	S-17	0.8	P-1	890
232	S-18	0.8	P-1	1340
233	S-19	0.8	P-1	630
234	S-20	0.8	P-1	205
235	S-21	0.8	P-1	143
236	S-22	0.8	P-1	113
237	S-23	0.8	P-1	85
238	S-24	0.8	P-1	57
239	S-25	0.8	P-1	68
240	S-17	0.8	P-3	17800
241	S-18	0.8	P-3	35800
242	S-19	0.8	P-3	21300
243	S-20	0.8	P-3	820
244	S-21	0.8	P-3	230
245	S-22	0.8	P-3	147
246	S-23	0.8	P-3	118
247	S-24	0.8	P-3	82
248	S-25	0.8	P-3	77
249	S-17	0.8	P-42	57000
250	S-18	0.8	P-42	134000
251	S-19	0.8	P-42	112000
252	S-21	0.8	P-42	2450
253	S-22	0.8	P-42	800
254	S-23	0.8	P-42	3250
255	S-26	0.8	P-42	43000
256	S-27	0.8	P-42	37000
257	S-28	0.8	P-42	71000
258	S-29	0.8	P-42	5800
259	S-30	0.8	P-42	375
260	S-31	0.8	P-42	650
261	S-32	0.8	P-42	2400
262	S-17	0.8	P-46	68000
263	S-18	0.8	P-46	13000
264	S-19	0.8	P-46	88000
265	S-21	0.8	P-46	2900
266	S-22	0.8	P-46	1400
267	S-23	0.8	P-46	2400

Table U
(Continued)

Example	Surfactant	Surfactant Concentration (wt.%)	Thickener	Brookfield Viscosity (cps) @ pH = 9.0
268	S-226	0.8	P-46	25000
269	S-227	0.8	P-46	38500
270	S-228	0.8	P-46	77000
271	S-229	0.8	P-46	7200
272	S-230	0.8	P-46	550
273	S-231	0.8	P-46	690
274	S-232	0.8	P-46	1775
275	Aerosol OT	0.0	P-4	50500
	Aerosol OT	0.1	P-4	93500
	Aerosol OT	0.2	P-4	42000
	Aerosol OT	0.4	P-4	11200
	Aerosol OT	0.8	P-4	3700
	Aerosol OT	1.0	P-4	7200
	Aerosol OT	2.0	P-4	10600

Examples 276-288

Co-Thickening with Solvents and Non-Solvents

Solvents and non-solvents added to an associative polymer solution influences the co-thickening effect. The results in Table W below show the co-thickening effect produced by the addition with thorough mixing of certain solvents and non-solvents identified in Table V below in the amounts identified in Table W to a 0.75% alkaline solution of an alkali soluble thickener identified in Table W as measured with a Brookfield Viscometer at 6 rpm at pH = 9.0.

Table V

Solvent Designation	Solvent
O-1	mineral spirits
O-2	butanol
O-3	Isobutanol
O-4	Isopropanol
O-5	2-Ethylhexanol
O-6	Butyl Carbitol
O-7	Butyl DiPropasol
O-8	Butyl Propasol
O-9	Propyl DiPropasol
O-10	Propyl Propasol
O-11	Methyl DiPropasol
O-12	Methyl Propasol

Table W

Example	Thickener	Solvent	Solvent Concentration (wt.%)	Solvent O-1 Concentration (wt.%)	Brookfield Viscosity (cps) @ pH = 9.0
276	P-3	O-6	5	0	29200
	P-3	O-6	10	0	865
	P-3	O-6	20	0	625
	P-3	O-6	40	0	720
	P-3	O-6	5	5	15400
	P-3	O-6	10	5	1125
	P-3	O-6	20	5	735
	P-3	O-6	40	5	780
	P-3	O-6	5	10	56500
	P-3	O-6	10	10	1050
	P-3	O-6	20	10	835
	P-3	O-6	40	10	832
	P-3	O-6	5	20	41500
	P-3	O-6	10	20	1625

Table W
(Continued)

Example	Thickener	Solvent	Solvent Concentration (wt.%)	Solvent O-1 Concentration (wt.%)	Brookfield Viscosity (cps) @ pH = 9.0
277	P-3	O-7	0	0	76000
	P-3	O-7	5	0	2150
	P-3	O-7	10	0	3700
	P-3	O-7	20	0	2000
	P-3	O-7	0	5	89000
	P-3	O-7	5	5	88000
	P-3	O-7	10	5	50000
	P-3	O-7	20	5	46500
	P-3	O-7	0	10	102400
	P-3	O-7	5	10	122000
	P-3	O-7	10	10	72000
	P-3	O-7	0	20	113000
	P-3	O-7	5	20	158000
	P-3	O-7	10	20	138000
278	P-3	O-8	5	0	1925
	P-3	O-8	10	0	1150
	P-3	O-8	20	0	2000
	P-3	O-8	40	0	6200
279	P-3	O-9	5	0	36000
	P-3	O-9	10	0	1200
	P-3	O-9	20	0	440
	P-3	O-9	40	O	1375
280	P-3	O-10	5	0	1375
	P-3	O-10	10	0	45500
	P-3	O-10	20	0	625
	P-3	O-10	40	0	510
281	P-3	O-11	5	0	36000
	P-3	O-11	10	0	20500
	P-3	O-11	20	0	4200
	P-3	O-11	40	0	550

Table W
(Continued)

Example	Thickener r	Solvent	Solvent Concentration (wt.%)	Solvent O-1 Concentration (wt.%)	Brookfield Viscosity (cps) @ pH = 9.0
282	P-3	O-12	0	0	76000
	P-3	O-12	5	0	45000
	P-3	O-12	10	0	24500
	P-3	O-12	20	0	5800
	P-3	O-12	40	0	675
	P-3	O-12	5	5	51500
	P-3	O-12	10	5	28500
	P-3	O-12	20	5	7100
	P-3	O-12	40	5	810
	P-3	O-12	5	10	61200
	P-3	O-12	10	10	33500
	P-3	O-12	20	10	6400
	P-3	O-12	40	10	950
	P-3	O-12	5	20	86800
	P-3	O-12	10	20	40500
	P-3	O-12	20	20	7100
	P-3	O-12	40	20	1350
283	P-14	O-7	0	0	150000
	P-14	O-7	5	0	1350
	P-14	O-7	10	0	4500
	P-14	O-7	20	0	7000
	P-14	O-7	0	5	140000
	P-14	O-7	5	5	120000
	P-14	O-7	10	5	78000
	P-14	O-7	0	5	140000
	P-14	O-7	5	10	158000
	P-14	O-7	10	10	124000
	P-14	O-7	0	20	136000
	P-14	O-7	5	20	152000
	P-14	O-7	10	20	142000

Table W
(Continued)

Example	Thickeneier	Solvent	Solvent Concentration (wt.%)	Solvent O-1 Concentration (wt.%)	Brookfield Viscosity (cps) @ pH = 9.0
284	P-3a	O-2	0	0	132600
	P-3a	O-2	5	0	17300
	P-3a	O-2	10	0	850
	P-3a	O-2	20	0	1425
	P-3a	O-2	40	0	4750
	P-3a	O-2	0	5	140000
	P-3a	O-2	5	5	67000
	P-3a	O-2	10	5	2500
	P-3a	O-2	20	5	3000
	P-3a	O-2	0	10	134000
	P-3a	O-2	5	10	33000
	P-3a	O-2	10	10	4000
	P-3a	O-2	20	10	4900
	P-3a	O-2	0	20	144000
	P-3a	O-2	5	20	49000
	P-3a	O-2	10	20	8000
285	P-3a	O-3	5	0	28500
	P-3a	O-3	10	0	880
	P-3a	O-3	20	0	1425
	P-3a	O-3	40	0	4600
	P-3a	O-3	5	5	80000
	P-3a	O-3	10	5	2950
	P-3a	O-3	20	5	3200
	P-3a	O-3	40	5	6200
	P-3a	O-3	5	10	78000
	P-3a	O-3	10	10	5200
	P-3a	O-3	20	10	6400
	P-3a	O-3	5	20	136000
	P-3a	O-3	10	20	20500

Table W
(Continued)

Example	Thickener	Solvent	Solvent Concentration (wt.%)	Solvent O-1 Concentration (wt.%)	Brookfield Viscosity (cps) @ pH = 9.0
286	P-3a	O-4	5	0	94000
	P-3a	O-4	10	0	29000
	P-3a	O-4	20	0	1050
	P-3a	O-4	40	0	850
	P-3a	O-4	5	5	107400
	P-3a	O-4	10	5	39000
	P-3a	O-4	20	5	1225
	P-3a	O-4	40	5	900
	P-3a	O-4	5	10	134000
	P-3a	O-4	10	10	41000
	P-3a	O-4	20	10	1350
	P-3a	O-4	40	10	1050
	P-3a	O-4	5	20	164000
	P-3a	O-4	10	20	33000
	P-3a	O-4	20	20	1825
	P-3a	O-4	40	20	1350
287	P-3a	O-5	5	0	93500
	P-3a	O-5	10	0	136000
	P-3a	O-5	20	0	178000
288	P-3a	O-7	5	0	2700
	P-3a	O-7	10	0	6100
	P-3a	O-7	20	0	11900

Althaough the invention has been illustrated by certain of the preceding exaamples, it is not to be construed as being limited thereby; but rathaer, the invention encompasses the generic area as hereinbefore discklosed. Various modifications and embodiments can be made without ‹ departing from the spirit and scope thereof.

Claims

1. A polymer comprising the reaction product of:

(A)) about 0-99.9 weight percent of one or more nonionic, cationnic, anionic or amphoteric monomers;

(B)) about 0-99.9 weight percent of one or more monoethylenicablly unsaturated monomers different from (A);

(C)) about 0.1-100 weight percent of one or more monoethylenicablly unsaturated macromonomers different from (A) and (B); and

(D)) about 0-20 weight percent or greater of one or more polyethylenicallyly unsaturated monomers different from (A), (B) and (C).

2.2. The polymer of claim 1 comprising the reaction product of:

(AA) about 1-99.9 weight percent of one or more alpha, beta-monoethyldenically unsaturated carboxylic acids;

(BB) about 0-98.9 weight percent of one or more monoethylenicablly unsaturated monomers different from (A);

(CC) about 0.1-99 weight percent of one or more monoethylenicablly unsaturated macromonomers different from (A) and (B); and

(DD) about 0-20 weight percent or greater of one or more polyethyleenically unsaturated monomers different from (A), (B) and (C).

3.3. The polymer of claim 1 comprising the reaction product of:

(AA) from 1 to about 99.9 weight percent of one or more nonionic nmonoethylenically unsaturated monomers; and

(B)) from about 0.1 to 99 weight percent of one or more monoethylenically unsaturated macromonomers different from (A).

4. A compound represented by the formula:

$$\begin{array}{l} \qquad\qquad\quad R^4 \\ \qquad\qquad\quad | \\ R^1\text{-}(OR^2)_z\text{-}R^3\text{-}C=CR^5R^6 \end{array}$$

wherein:

R^1 is a monovalent residue of a substituted or unsubstituted complex hydrophobe compound;

each R^2 is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue;

R^3 is a substituted or unsubstituted divalent hydrocarbon residue;

R^4, R^5 and R^6 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue; and

z is a value of 0 or greater.

5. A compound represented by the formula selected from:

$$\begin{array}{l} R_1\text{-}(O\text{-}CH_2)_a \\ \qquad\qquad \diagdown \\ \qquad\qquad\quad R_3\text{-}(OR_4)_x\text{-}(OR_5)_y\text{-}OR_6 \\ \qquad\qquad \diagup \\ R_2\text{-}(O\text{-}CH_2)_b \end{array}$$

wherein R_1 and R_2 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue, R_3 is a substituted or unsubstituted divalent or trivalent hydrocarbon residue, each R_4 is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, each R_5 is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, R_6 is hydrogen, a substituted or unsubstituted monovalent hydrocarbon residue or an ionic substituent, a and b are the same or different and are a value of 0 or 1, and x and y are the same or different and are a value of 0 or greater; provided (i) at least two of R_1, R_2, R_3, R_4, R_5 and R_6 are a hydrocarbon residue having greater than 2 carbon atoms in the case of R_1, R_2 and R_6 or having greater than 2 pendant carbon atoms in the case of R_3, R_4 and R_5, (ii) at least one of R_4 and R_5 is other than $-CH_2CH_2-$ when R_1 and R_2 are nonylphenyl, R_3 is $>CH-$, R_6 is hydrogen or SO_3, a is a value of 1, b is a value of 1, and at least one of x and y is a value of 1 or greater, and (iii) R_4 is $-CH_2CH_2-$ and x is a value of at least 2 when R_1 is hexadecyl, R_2 is tetradecyl, R_3 is $>CH-$, at least one R_5 is $-CH_2CH(\text{tetradecyl})-$, R_6 is hydrogen, y is a value of 1 or greater, a is a value of 1, and b is a value of 0; and

$$
\begin{array}{l}
R_7\text{-}(OCH_2)_d\text{-}R_9\text{-}(OR_{10})_f\text{-}OR_{11} \\
\qquad\qquad\quad | \\
\qquad\qquad\quad R_{15} \\
\qquad\qquad\quad | \\
R_8\text{-}(OCH_2)_e\text{-}R_{12}\text{-}(OR_{13})_g\text{-}OR_{14}
\end{array}
$$

wherein R_7 and R_8 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue, R_9 and R_{12} are the same or different and are a substituted or

unsubstituted divalent or trivalent hydrocarbon residue, each R_{10} is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, each R_{13} is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, R_{11} and R_{14} are the same or different and are hydrogen, a substituted or unsubstituted monovalent hydrocarbon residue or an ionic substituent, R_{15} is a substituted or unsubstituted divalent hydrocarbon residue, d and e are the same or different and are a value of 0 or 1, and f and g are the same or different and are a value of 0 or greater; provided at least two of R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14} and R_{15} are a hydrocarbon residue having greater than 2 carbon atoms in the case of R_7, R_8, R_{11} an R_{14} or having greater than 2 pendant carbon atoms in the case of R_9, R_{10}, R_{12}, R_{13} and R_{15}.

6. The polymers of claims 1, 2 and 3 wherein said monoethylenically unsaturated macromonomer is represented by the formula depicted in claim 4.

7. The polymers of claim 6 wherein the substituted or unsubstituted complex hydrophobe compound is represented by the formula selected from:

$$\begin{array}{l} R_1\text{-}(O\text{-}CH_2)_a \\ \qquad\qquad\quad \diagdown \\ \qquad\qquad\qquad R_3\text{-}(OR_4)_x\text{-}(OR_5)_y\text{-}OR_6 \\ \qquad\qquad\quad \diagup \\ R_2\text{-}(O\text{-}CH_2)_b \end{array}$$

wherein R_1 and R_2 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue, R_3 is a substituted or unsubstituted divalent or trivalent hydrocarbon residue,

each R_4 is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, each R_5 is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, R_6 is hydrogen, a substituted or unsubstituted monovalent hydrocarbon residue or an ionic substituent, a and b are the same or different and are a value of 0 or 1, and x and y are the same or different and are a value of 0 or greater; provided at least two of R_1, R_2, R_3, R_4, R_5 and R_6 are a hydrocarbon residue having greater than 2 carbon atoms in the case of R_1, R_2 and R_6 or having greater than 2 pendant carbon atoms in the case of R_3, R_4 and R_5; and

$$
\begin{array}{l}
R_7\text{-}(OCH_2)_d\text{-}R_9\text{-}(OR_{10})_f\text{-}OR_{11} \\
\qquad\qquad\quad | \\
\qquad\qquad\quad R_{15} \\
\qquad\qquad\quad | \\
R_8\text{-}(OCH_2)_e\text{-}R_{12}\text{-}(OR_{13})_g\text{-}OR_{14}
\end{array}
$$

wherein R_7 and R_8 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue, R_9 and R_{12} are the same or different and are a substituted or unsubstituted divalent or trivalent hydrocarbon residue, each R_{10} is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, each R_{13} is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, R_{11} and R_{14} are the same or different and are hydrogen, a substituted or unsubstituted monovalent hydrocarbon residue or an ionic substituent, R_{15} is a substituted or unsubstituted divalent hydrocarbon residue, d and e are the same or different and are a value of 0 or 1, and f and g are the same or different and are a value of 0 or greater; provided at least two of R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14} and R_{15} are a hydrocarbon residue having greater than 2 carbon atoms in the case of

R_7, R_8, R_{11} an RR_{14} or having greater than 2 pendant carbon atoms in the case of R_9, R_{10}, RR_{12}, R_{13} and R_{15}.

8. The compound of claim 4 wherein the substituted or unsubstituted coomplex hydrophobe compound is represented by the formula selected l from:

$$
\begin{array}{l}
R_1\text{-}(O\text{-}CH_2)_a \\
\qquad\qquad \backslash\backslash \\
\qquad\qquad\quad R_3\text{-}(OR_4)_x\text{-}(OR_5)_y\text{-}OR_6 \\
\qquad\qquad // \\
R_2\text{-}(O\text{-}CH_2)_b
\end{array}
$$

wherein R_1 and FR_2 are the same or different and are hydrogen or a substituted or unnsubstituted monovalent hydrocarbon residue, R_3 is a substituted or unnsubstituted divalent or trivalent hydrocarbon residue, each R_4 is the sanme or different and is a substituted or unsubstituted divalent hydrocarrbon residue, each R_5 is the same or different and is a substituted or unnsubstituted divalent hydrocarbon residue, R_6 is hydrogen, a substtituted or unsubstituted monovalent hydrocarbon residue or an ionic substitituent, a and b are the same or different and are a value of 0 or 1, and x annd y are the same or different and are a value of 0 or greater; provided ((i) at least two of R_1, R_2, R_3, R_4, R_5 and R_6 are a hydrocarbon residdue having greater than 2 carbon atoms in the case of R_1, R_2 and R_6 or r having greater than 2 pendant carbon atoms in the case of R_3, R_4 and R_5, , (ii) when R_1 is hexadecyl, a is a value of 1, R_2 is tetradecyl, b is a vvalue of 0, R_3 is $>$CH-, R_4 is $-CH_2CH$(tetradecyl)-, x is a value of 1, R_5 is $-CCH_2CH_2-$, y is a value of 34, R_6 is hydrogen and z is a value of 0, then thhe $-R^3-(R^4)C=CR^5R^6$ portion of the compound is other than the residue (of maleic anhydride, and (iii) when R_1 is hexadecyl, a is a value of 1, R_2 is s tetradecyl, b is a value of 0, R_3 is $>$CH-, R_4 is

$-CH_2CH$(tetradecyl)-, x is a value of 1, y is a value of 0, R_6 is hydrogen and z is a value of 344, then the $-R^3-(R^4)C=CR^5R^6$ portion of the compound is other than the residue of maleic anhydride; and

$$
\begin{array}{l}
R_7\text{-}(OCH_2)_d\text{-}R_9\text{-}(OR_{10})_f\text{-}OR_{11} \\
\qquad\qquad\quad | \\
\qquad\qquad\quad R_{15} \\
\qquad\qquad\quad | \\
R_8\text{-}(OCH_2)_e\text{-}R_{12}\text{-}(OR_{13})_g\text{-}OR_{14}
\end{array}
$$

wherein R_7 and R_8 are the same or different and are hydrogen or a substituted or unsubstituted monovalent hydrocarbon residue, R_9 and R_{12} are the same or different and are a substituted or unsubstituted divalent or trivalent hydrocarbon residue, each R_{10} is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, each R_{13} is the same or different and is a substituted or unsubstituted divalent hydrocarbon residue, R_{11} and R_{14} are the same or different and are hydrogen, a substituted or unsubstituted monovalent hydrocarbon residue or an ionic substituent, R_{15} is a substituted or unsubstituted divalent hydrocarbon residue, d and e are the same or different and are a value of 0 or 1, and f and g are the same or different and are a value of 0 or greater; provided at least two of R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14} and R_{15} are a hydrocarbon residue having greater than 2 carbon atoms in the case of R_7, R_8, R_{11} and R_{14} or having greater than 2 pendant carbon atoms in the case of R_9, R_{10}, R_{12}, R_{13} and R_{15}.

9. The polymers of claim 7 and the compound of claim 8 wherein (i) at least one of R_1, R_2, R_7 and R_8 is a hydrocarbon radical represented by the formula:

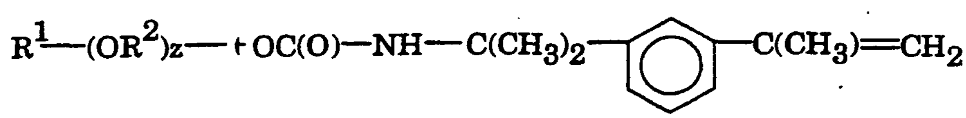
$$\begin{array}{lll} R_{16}\text{-}(O\text{-}CH_2)_h & & \\ & \diagdown & \\ & & R_{18}\text{-} \\ & \diagup & \\ R_{17}\text{-}(O\text{-}CH_2)_i & & \end{array}$$

wherein R_{16} andd R_{17} are the same or different and are hydrogen or a substituted or unnsubstituted monovalent hydrocarbon residue, R_{18} is a substituted or u unsubstituted divalent or trivalent hydrocarbon residue, and h annd i are the same or different and are a value of 0 or 1; and/or (ii) at leeast one of R_4, R_5, R_{10} and R_{13} is a hydrocarbon radical representtted by the formula:

$$\text{-CHH}[(OR_{19})_j OR_{20}]\text{-}$$

wherein each R_{19} is the same or different and is a substituted or unsubstituted divivalent hydrocarbon residue, R_{20} is hydrogen, a substituted or unnsubstituted monovalent hydrocarbon residue or an ionic substituent, and j is a value of 0 or greater.

10. The polymers of claim 7 and the compound of claim 8 in which said monoethylenically unsaturated macromonomer aand compound are represented by the formula selected from:



$$
\begin{array}{l}
\qquad\qquad\qquad\qquad\qquad\qquad R^4 \\
\qquad\qquad\qquad\qquad\qquad\qquad | \\
R^1\text{-}(OR^2)_z\text{-}CH_2CCHCH_2OCH_2C{=}CH_2 \\
\qquad\qquad\qquad\quad | \\
\qquad\qquad\qquad (OOR_{19})_jOH
\end{array}
$$

$$
\begin{array}{l}
\qquad\qquad\qquad\quad R^4 \\
\qquad\qquad\qquad\quad | \\
R^1 - (OR^2)_z - OCC(O)\text{-}C{=}CH_2
\end{array}
$$

wherein R^1, R^2, , R^4 and z are as defined in claim 4, and R_{19} and j are as defined in claaim 9.

11. An aqueous latex containing the solubilized or neutralized aqueaeous polymer of claim 1.

12. A process of thickening an aqueous system comprising addiring to the system a polymer of claim 1 and at least partially solubililizing or neutralizing said polymer.

13. The process of claim 12 wherein the system is thickened furtheer by the addition of an effective amount of surfactant, solvent or non-sgolvent.

14. An aqueous polymer emulsion useful as a thickening agentt in aqueous compositions when the polymer is

dissolved thereinn, which comprises water and emulsified polymer particles comprisising the polymer of claims 1, 2 or 3.

15. In a latex paint composition comprising latex polymer, water, ppigment, and thickener, the improvement which comprises havingg as at least a portion of the thickener dissolved therein a polymerr comprising the polymer of claims 1, 2 or 3.

16. In an aqueous composition comprising water and thickener, the impprovement which comprises having as at least a portion of the thiickener dissolved therein a polymer comprising the polymer of claimss 1, 2 or 3.

17. A derivative of the compound of claims 4 or 5.

18. An emulsifier, dispersant, stabilizer, wetting agent, a copolymeerizable monomer in polymerization reaction or a latex binder compprising the compound of claims 4 or 5.

19. A latex composition containing water, latex polymer and the c compound of claims 4 or 5.

20. A method for the alkoxylation of a complex hydrophobe compound having at least one active hydrogen comprising alkoxyylating the complex hydrophobe compound of claim 5 with an alkylenoe oxide in the presence of a catalyst to produce alkoxylates of thee complex hydrophobe compound under alkoxylation conditions.

21. A method for preparing alkoxylation product mixtures having a a narrow distribution of species with at least one specie comprisingg at least about 10 weight percent of the product

mixture compprising contacting a complex hydrophobe compound of claim 5 havingg at least one active hydrogen with an alkylene oxide in the presence o of a catalytically effective amount of catalyst under alkoxylation cconditions sufficient to provide a product mixture having at leastst one alkoxylation specie comprising at least about 10 weight percentt of the mixture.

222. The method of claim 20 further comprising derivatizing thhe product in which the derivatizing reaction comprises an oxidation, c carboxylation, reduction, hydrogenation, dehydrogenatiion, condensation, amination, esterification, etherification, silylation, alkylation or acylation reaction.

IN[redacted]NATIONAL SEARCH REPORT

[redacted]onal Application No
[redacted]/US 93/04872

A. CLASSIFICATION OF SUBJECT MATTTTER
IPC 5 C08F220/28 C08BF220/04 C09D4/00 C08F246/00

According to International Patent Classificationon (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classificatiation system followed by classification symbols)
IPC 5 C08F C09D C07C

Documentation searched other than minimum m documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the interrnational search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RRELEVANT

Category *	Citation of document, with indicatation, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 029 872 ((EVANI ET AL.) 14 June 1977 see the whole ddocument	1,3,4,6, 16-18
X	EP,A,0 173 109 ((DESOTO) 5 March 1986 cited in the appplication see claims 1-10) & US,A,4 514 5532	1-8, 10-19
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[X] Further documents are listed in the contintinuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"&" document member of the same patent family

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Date of the actual completion of the internationonal search	Date of mailing of the international search report
4 November 1993	11. 11. 93

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	ANDRIOLLO, G

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INTERNATIONAL SEARCH REPORT

International Application No
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